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during

Third Western Regional Conference, The Chemical Institute of Canada
University of Alberta, Edmonton, September 13 - 15, 1956

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Research Council of Alberta
87th Avenue and 114th Street
Edmonton, Alberta
1957

FOREWORD

During the Third Western Regional Conference of The Chemical Institute of Canada, held at the University of Alberta, Edmonton, September 13 - 15, 1956, a symposium was held on "The Occurrence and Chemical Utilization of Light Hydrocarbons". Five papers were presented at the symposium by representatives of industry, the University of Alberta, and the Research Council of Alberta.

Since the five papers represented a comprehensive, even though brief, review of many aspects of the occurrence and chemical utilization of light hydrocarbons, it was thought desirable to reproduce these papers together as a "separate", as this would enhance the value of each of the papers and make them much more convenient for reference. The authors were contacted and expressed full agreement with the plan.

Due to the immense reserves of light hydrocarbons in Alberta, presently under development, the information contained in these papers is, obviously, of particular interest and value to this province. Therefore, it is appropriate that the Research Council of Alberta, which is vitally interested in the development of Alberta's natural resources, should undertake to reproduce these papers. They are being issued as Mimeographed Circular No. 23.

EDITORIAL NOTE

The papers have not been edited and are reproduced in the form presented by the authors.

Reprinting of material from these papers is welcomed, provided that appropriate reference is given to author, title of paper, and this circular.

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THE RESERVES OF LIGHT HYDROCARBONS IN WESTERN CANADA

by George W. Govier*

It is a pleasure for me to open the symposium on the petrochemical industry in Western Canada by discussing the reserves of the light hydrocarbons. Alberta, in particular, and all of Western Canada have been endowed with a plentiful supply of crude oil and natural gas, the two primary sources of petrochemical raw materials. Hydrocarbons from these two sources are already being used in important chemical operations in Alberta, and several new projects are either under construction or in the serious planning stage. Western Canada is undoubtedly experiencing an industrial revolution in which oil and gas and products derived from them are playing a key role. In this symposium we are interested in the petrochemical side of this development, and my own function is to show what is available here in the West as hydrocarbon fuel and raw material. Although crude oil and natural gas are the ultimate sources, there are a number of ways in which fuel gas and raw materials are obtained from oil and gas.

Natural Gas

Considering natural gas first, it should be recognized that this is a complex mixture of methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane, traces of higher hydrocarbons, water vapor, nitrogen, and (often) hydrogen sulphide and carbon dioxide. While in all natural gases the proportions of the hydrocarbon constituents decrease with increasing molecular weight, there is a tremendous variation from gas to gas in the content of the constituents. Gases which are high in methane and low in propane and higher components are

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* Head, Department of Chemical and Petroleum Engineering, University of Alberta, and Member, The Petroleum and Natural Gas Conservation Board, Province of Alberta.

customarily known as dry gases - the word "dry" referring to their lack of liquifiable hydrocarbons. Gases which contain commercially recoverable quantities of propane and higher hydrocarbons are all called "wet gases". These may be found quite separate from crude oil but often they are associated with it in the underground formation. All crude oils, under the entrapping pressure of the reservoir, contain natural gas dissolved in them. The quantity and the composition of such "solution" gas depends upon the reservoir pressure and the nature of the crude oil. Most solution gases, however, are of the wet variety and solution gas, produced unavoidably with oil, is an important source of wet gas. Often too, natural gas is found in contact with and immediately overlying an underground accumulation of crude oil. This "gas cap gas", as it is called, is usually of a composition intermediate between the non-associated dry gas and the wet solution gas. Another intermediate grade of gas is that produced from what are known as condensate reservoirs. The Pincher Creek and Jumping Pound fields in Alberta are examples. Here the petroleum occurs in the underground reservoir in the form of a single phase above its critical pressure or temperature. Reduction of pressure accompanying production from such reservoirs causes retrograde condensation resulting in the production at the surface of condensate - a light crude oil, and condensate gas which is usually relatively dry.

We see, therefore, that natural gas of widely varying composition may be produced from dry gas fields, wet gas fields, solution in oil fields, gas caps in oil fields and from condensate fields. I have indicated the composition of three typical gases in Table I. The Viking-Kinsella gas is dry and sweet. The Pincher Creek gas is relatively dry and sour - i.e. it contains a lot of hydrogen sulphide. The Redwater gas is wet and sour. All natural gases except those

which are dry and sweet require processing at or near their points of production. There are several reasons for this - to render the gas transportable by pipeline, to adjust heating value to the level desired by the market, to remove hydrogen sulphide and to recover, for separate use or sale, the economically recoverable higher hydrocarbons or sulphur. This processing results in the production of residue gas - a dry sweet gas of about 1000 BTU heating value, relatively pure propane and butane, and natural gasoline. Ethane could be recovered but is not unless a special market for it exists.

Crude Oil

Turning now to crude oil - even after it is robbed of most of its solution gas it is an important source of light hydrocarbons. In refinery operations the relatively small amount of dissolved gas remaining in the crude oil is augmented by decomposition products of thermal and catalytic cracking. The amount and composition of the remaining dissolved gas depends upon the nature of the crude oil and the extent to which it has been exposed to the atmosphere and allowed to weather. The amount and composition of the gaseous products of cracking are dependent in a most complex way on the nature of the crude oil, and the pressure, temperature, time and catalyst conditions of the refinery processing. For these reasons it will be clear that it is difficult to define the amount and composition of refinery gases. A survey of refiners in Western Canada has given useful data in this connection. Yields varied from an isolated low of 30, to a high of 434 cubic feet per barrel of crude oil throughput. The yields and approximate compositions of refinery gas for four typical refineries in Western Canada are given in Table II. The refinery gases will be seen to be of much different composition than the natural gases. They contain hydrogen, methane,

ethane, ethylene, propane, propylene, butanes and butylenes. They are much lower in methane and much higher in the higher hydrocarbons, and they contain unsaturated gases not present in natural gases. Because of the high proportion of propane and higher hydrocarbons refinery gases are not piped long distances and, like wet natural gases, must be processed and are only available at or near the refinery. In fact, the processing of such gases for the recovery of some of the propane and most of the butane is usually integrated with the rest of the refinery operation.

Natural Gas Reserves

Reserve estimates and production forecasts of the available hydrocarbons are of the utmost importance not only in the planning of new petrochemical ventures, but in the intelligent operation of existing plants. Reserves of natural gas hydrocarbons are derived from estimates of the reserves of natural gas in the ground, the proportion estimated to be producible and the composition of the gas. The producible gas is raw gas and, as I have mentioned previously, it nearly always requires processing. The residue gas resulting from the processing may be anywhere from about 50 to over 90 percent of the original raw gas, depending on the composition of the raw gas. The yields of propane and butanes vary in the same way and also depend upon the available market.

Table III presents a summary of reserve estimates for the most important source fields of natural gas in Western Canada. The Alberta figures are unofficial or preliminary revisions to December 31, 1955 of figures published by the Petroleum and Natural Gas Conservation Board as of June 30, 1955. The British Columbia figures are based on estimates of Ralph E. Davis of November 14, 1955. The Saskatchewan figures are

taken from the 1955 Petroleum and Natural Gas Statistical Handbook published by the Saskatchewan Department of Mineral Resources.

All fields having estimated recoverable raw gas reserves in excess of 100 BCF are listed separately as well as several smaller ones of special interest. Total figures for "Other Fields" are given to complete the tabulation. The estimates show the recoverable raw gas and the available dry or residue gas which may be derived from it by processing. For those dry gases which contain 5 percent or more of ethane the amount of ethane which might be recovered is also estimated. Here a 40 percent recovery has arbitrarily been assumed. (The ethane which might be recovered has not been deducted from the available dry gas figure.) Propane and butane recoveries of 50 and 90 percent respectively were assumed to get the recoverable quantities of these components. No estimates of ethane, propane or butane recoveries from the "Other Fields" were made, but little recovery would be expected.

The reserves of the raw gas, the dry gas and the recoverable ethane are given in billions of cubic feet; those of the propane and butane are in millions of Imperial gallons. Billions of cubic feet of gas are hard to visualize. Perhaps it would help if I told you that a billion cubic feet of dry gas is thermally equivalent to about 50,000 tons of good grade bituminous coal or some 150,000 barrels of fuel oil.

The present dominant position of Alberta is clear from the relative numbers of fields and the subtotals for each province. The dry gas reserves are in the ratio of about 40:4:1 for Alberta-British Columbia-Saskatchewan. The ratio of propane and butane reserves for Alberta and British Columbia is about 12:1 and 10:1 respectively. It should be emphasized that these figures are estimates based upon available information at the present time. In many cases, such as for

Viking-Kinsella, for Leduc-Woodbend and for other well developed areas, the estimates will be very good. In other cases such as for Pembina and especially for Savanna Creek and Sarcee, where development is far from complete, the figures must be considered tentative. In all cases, however, the reserves are those considered pretty well proven, so the estimates are thought to be conservative.

I would not like to leave this topic without some reference to the rate at which these reserves have been growing and to what is expected in the future. Over the past ten years the reserves of available dry gas in Alberta have increased by about 12 trillion cubic feet or at the average rate of 1200 billion cubic feet per year. For most of the ten year period the annual rate was higher. This growth occurred over a period of unfavorable market for gas and when the incentive to discover and develop new gas reserves was low. Looking into the future one may reasonably expect an increasing interest in the development of gas reserves and an acceleration of exploration activity. The remaining available dry or residue gas reserves in Alberta are expected to grow from the present 17 odd trillion cubic feet to about 22 in 1960 and to over 30 trillion cubic feet in 1970.

Reserves From Crude Oil Refining

The reserves of light hydrocarbons derived from crude oil refining may be estimated in either of two ways. One way is from an estimate of the recoverable reserves of crude oil and figures representing the average yield and composition of refinery gas per barrel of crude oil. The difficulty here is that Western Canada's crude oil goes far beyond Western Canada. In 1955, of Alberta's daily average production of some 302,000 barrels, some 57,000 were refined in Alberta, 53,000 in British Columbia, 35,000 in Saskatchewan, 17,000 in Manitoba,

100,000 in Ontario and 40,000 in the United States. This year and future years will see an even greater proportion of Alberta's increasing production move to Eastern Canada and the United States. Thus an estimate of refinery gases based upon Western Canada's total crude oil reserves is not too helpful in a consideration of Western Canada's petrochemical potentialities.

Another approach and the one I have used is to base the estimate on Western Canada's refining capacity, assuming, as is certainly reasonable, that reserves will be available to operate the refineries for a long time into the future. One really should project refinery capacity into the future for there is no doubt that Western Canada's present capacity of some 212,000 barrels per day will increase, probably doubling in the next 25 or 30 years. On the other hand refinery technology is changing rapidly too, and who is to say what the yield of refinery gases will be in the future. The safest procedure seems to be to take the present refinery capacity and the present yields and to estimate light hydrocarbon totals for, say, a 25-year period. This is what I have done in Table IV. Western Canada has been divided into its major refining centers and the 25-year cumulative figures for total gas, ethane and ethylene, propane and propylene, and butanes and butylenes have been calculated. The C_2 hydrocarbons have been taken at 10 percent of the total gas, representing a recovery of from 50 to 75 percent depending upon the refinery gas composition. The C_3 hydrocarbons were estimated on the basis of 25 percent of the total gas, which reflects a 75 to 90 percent recovery; the C_4's at 35 percent of the total gas, equivalent to an 80 to 90 percent recovery.

Comparing Tables III and IV it is clear that natural gas is a much larger source of all the hydrocarbons, but that very important quantities of C_3 and C_4 compounds are available at refineries. Also,

almost equal quantities of the refinery-derived compounds are available in each province and in each large refining center. Differential growth rates will modify this, but hardly to the extent present in the case of the natural gas derived hydrocarbons.

Rate of Production

The daily rate of production of the light hydrocarbons may be estimated with fair precision a few years into the future by detailed consideration of individual fields and individual refineries. The Conservation Board has done this in the case of the natural gas producing fields, but not for the refineries. In both cases, however, a fairly good idea of the daily production rates of the near future (all fields producing) may be obtained by dividing the reserve figure by 8,000 to 10,000. This assumes the reserve will be produced in a period of 22 to 28 years. (In the case of the refinery figures this just reverses the original calculation of the reserve.) My own way of doing this is to shift the decimal point of a reserve figure one point to the left and to convert billions to millions and millions to thousands. For example, in the case of Pincher Creek the reserve of 1900 billion cubic feet of dry gas becomes an average rate of 190 or, say, 200 million cubic feet per day; the propane and butane reserves of 365 and 500 million gallons become production rates of 36 - 40 and 50 - 55 thousand gallons per day. Similarly from Table IV, the Edmonton area productions of total refinery gas, C_2's, C_3's and C_4's would become about 7 and 0.7 million cubic feet per day and about 41 and 69 thousand gallons per day. This is a crude procedure but not too bad for orientation purposes.

Present Use and Commitments of the Light Hydrocarbons

It is not my job today to discuss the uses to which light hydrocarbons produced in Western Canada are now being put nor their commitments into the future. On the other hand, I do not wish to convey the

idea that all of these hydrocarbons are here awaiting new chemical industry. Much of the now available dry or residue gas is under contract to utility companies, industry, and export, but a good deal is available for new industrial use. Only surplus gas is to be exported from Alberta, and future Alberta requirements have been considered in the calculation of what is surplus. With respect to ethane much of that from Leduc-Woodbend is now being used here in Edmonton by Canadian Industries Limited, but no ethane recovery is being carried out elsewhere. Propane recovered from natural gas serves the L.P.G. industry - in the immediate past it has been in short supply in the winter but long in the summer. New plants soon to be in operation will provide year round surpluses. Canadian Chemicals Limited obtain butanes from Leduc-Woodbend but substantial surpluses are available elsewhere and production volumes will soon increase.

On the refinery gas side, there is partial recovery of both C_3 and C_4 hydrocarbons for separate sale, polymerization, alkylation and blending purposes, but about two-thirds of the total gas is being used as refinery fuel which could be replaced with dry natural gas or bunker fuel if there were a demand for these hydrocarbons. The demand could come from the refiners themselves through increased polymerization capacity or large scale alkylate production. On the other hand the C_3 and C_4 hydrocarbons could, as they do in the Sarnia and Houston areas, form the basis of petrochemical manufacture.

Conclusion

All of Western Canada has petrochemical raw materials available. Alberta and to a lesser extent British Columbia are doubly blessed with both natural gas and refinery sources. In Alberta, in particular, the reserves are extremely large and the production rates will soon be pro-

portionately so. If availability of fuel gas and raw materials were the only consideration, the West would certainly be the petrochemical center of Canada. Other speakers will deal with products, processing methods and certain economic factors of the petrochemical industry. These all have their influence on plant location, but when low cost fuel gas and hydrocarbon raw materials are important Western Canada has a decided advantage.

Table I

ANALYSES

TYPICAL RAW NATURAL GASES

1	2	3	4
	DRY SWEETGAS	CONDENSATE H.P.SEPARATOR GAS(4)	OILFIELD L.P. SEPARATOR GAS(5)
Field	Viking-Kinsella	Pincher Creek	Redwater
Zone	Viking	Rundle	Leduc (D3)
Composition			
Methane	89.4	74.1	59.3
Ethane	1.73	5.52	16.6
Propane	0.81	1.28	9.7
i-Butane	0.14	0.20	1.4
n-Butane	0.22	0.51	2.8
Pentanes Plus	0.21	0.54	0.9
Nitrogen (1)	7.50	2.72	2.5
Carbon Dioxide	0	6.60	4.0
Hydrogen Sulphide	0	8.50	2.8
Total	100.00	100.00	100.0
GPM(2)			
Propane	0.181	0.287	2.17
Butanes	0.043	0.184	1.09
Pentanes Plus	0.066	0.181	0.30
Total	0.340	0.652	3.56
GHV(3)	956	1060	1329

(1) by difference
(2) Imp. gals per MSCF as sampled (14.4 psia, 60°F)
(3) Gross heating value BTU per SCF (14.4psia, 60°F., moisture and acid gas free)
(4) Separator at 800 psig.
(5) Separator at 30 psig.

Table II

ANALYSES

TYPICAL REFINERY GASES

1	2	3	4	5
Refiner	A	B	C	D
Type of Refining	Catalytic Cracking	Thermal Cracking	Thermal and Catalytic Cracking	Thermal and Catalytic Cracking
Yield, CF/Bbl	238	234	172	198
Composition				
Hydrogen and Methane	20.4	26.5	17.0	16.2
Ethane	7.9	19.0	8.5	12.4
Ethylene	8.0	5.0	2.9	2.2
Propane	11.7	20.1	21.6	28.8
Propylene	17.5	10.4	12.7	10.1
Butanes	15.0	12.5	25.0	23.0
Butylenes	19.5	6.5	12.3	7.3
Total	100.0	100.0	100.0	100.0

Table III

RESERVES OF LIGHT HYDROCARBONS FROM NATURAL GAS

Dec. 31, 1955

1	2	3	4	5	6
Field	Recoverable Raw Gas BCF	Available Dry Gas BCF	Recoverable Ethane (1) BCF	Recoverable Propane (2) MMG	Recoverable Butanes (3) MMG
ALBERTA					
Acheson	117	54	3.5	90	45
Bonnie Glen	809	526	46	700	588
Cessford	1112	1057	-	-	-
Erskine	32	27	0.9	12.5	10.9
Etzikom	131	125	-	-	-
Fairydell-Bon Accord	102	97	-	-	-
Fenn-Big Valley	122	84	5	228	161
Ft. Saskatchewan	146	131	-	-	-
Gilby	200	172	-	64	49
Golden Spike	130	101	7.5	152	96
Gordondale	188	179	-	-	-
Harmattan-Elkton	720	576	22	215	210
Homeglen-Rimbey	874	700	27	288	209
Jumping Pound	648	529	-	-	-
Leduc-Woodbend	1900	880	42	650	505
Medicine Hat	914	822	-	-	-
Morinville	118	112	-	-	-
Nevis	631	510	13	3.5	2.6
Okotoks	338	135	-	-	-
Pembina	1200±	900±	40±	1100±	900±
Pendant D'Oreille	159	150	-	-	-
Pincher Creek	2700	1900	-	365	500
Pouce Coupe	220	209	-	-	-
Pouce Coupe South	173	165	-	-	-
Princess	180	168	-	-	-
Provost	568	540	-	-	-
Redwater	137	92	9.6	325	205
Sarcee	190	150	-	-	-
Savanna Creek	190	140	-	-	-
Stettler	22	14	1	53	28
Sturgeon Lake	26	17	0.8	18	16
Sturgeon Lake S.	170	110	4.8	108	95
Tangent	180	170	-	-	-
Turner Valley	490	350	13	102	84
Viking-Kinsella	600	570	-	-	-
Westlock	210	200	-	-	-
Westerose	190	148	11	198	228
Whitelaw	115	110	-	-	-
Windfall	150	105	-	75	75
Wizard Lake	128	92	8	125	105
Other Fields	4000	3600	-	-	-
Subtotals	21,200 (say)	16,700 (say)	250 (say)	4,900 (say)	4,000 (say)

Table III
(Continued)

BRITISH COLUMBIA					
Buick Creek	380	356			
Blueberry Mountain	96	90		Individual field details not available	
Fort St. John	890	833			
Nig Creek	150	134			
Other Fields	437	398			
Subtotal	2000 (say)	1900 (say)	30 (say)	390	420
SASKATCHEWAN					
Coleville-Smiley	-	164			
Hatton	-	133		Details not available but recoveries would be small	
Other Fields	-	128			
Subtotal	500 (say)	425	-	-	-
ALBERTA - BRITISHCOLUMBIA-SASKATCHEWAN					
Grand Total	23,700 (say)	19,000 (say)	280 (say)	5,300 (say)	4,400 (say)

(1) At 40 percent where ethane above 5%; not deducted from available dry gas
(2) At 50 percent
(3) At 90 percent

Table IV

RESERVES OF LIGHT HYDROCARBONS
FROM CRUDE OIL REFINING

(Basis 25 year cumulative Figures on Dec. 31, 1955
Rated Refining Capacity and Estimated Average Yields)

1 Area	2 Refining Capacity BPD	3 Total Gas Yield CF/BBL	4 25 Year Total Gas BCF	5 Ethane(1) Ethylene BCF	6 Propane(2) Propylene MMG	7 Butanes(3) Butylenes MMG
ALBERTA						
Calgary	15700	200±	28	2.8	157	267
Edmonton	41300	200±	74	7.4	415	695
Other Areas	23000	100±	20	2.0	110	187
Subtotal	80000		122	12.2	682	1149
BRITISH COLUMBIA						
Vancouver	59000	150±	78	7.8	440	730
Other Areas	7500	150±	10	1.0	56	93
Subtotal	66500		88	8.8	496	823
SASKATCHEWAN						
Moose Jaw	17500	200±	31	3.1	175	294
Regina	35500	200±	63	6.3	354	588
Other Areas	13300	150±	17.5	1.8	100	163
Subtotal	66300		112	11.2	629	1045
ALBERTA - BRITISH COLUMBIA - SASKATCHEWAN						
Grand Total	212,800	173	322	32.2	1807	3017

(1) Taken at 10% of total gas (50-75% recovery)
(2) Taken at 25% of total gas (75-90% recovery)
(3) Taken at 35% of total gas (80-90% recovery)

A NEW PETROCHEMICAL DEVELOPMENT

by E. J. Buckler* and H. Leverne Williams*

Introduction

During 1955 and 1956 technical news articles and publications appeared which indicated that a major advance had been achieved in polymer science, particularly with reference to hydrocarbon polymers. Due credit and priority will have to be unravelled by chemical historians ten years hence when all current work is published. At present, it appears that the pioneering work was carried out by groups in Germany and in the United States, working along different lines. In Germany, fifteen years' study on catalytic effects of organo-metallic compounds at the Max Planck Institute for Coal Research at Mülheim under Professor Karl Ziegler (1,2) began to yield patentable results starting in 1950 and reaching large proportions by 1954. These have been extended with spectacular success by Professor Giulio Natta (3), Institute Politecnico de Milano, in association with Societa Montecatini in Italy. In the United States, independent work by the Standard Oil Company of Indiana and Phillips Petroleum Company on solid oxide catalysts yielded patentable results, particularly in 1954 (4) and 1955 (5) respectively. Other companies also received valuable patents in the field (6).

The outcome of these advances is two fold. Firstly, catalysts have been evolved which will form solid polymer from simple hydrocarbons such as propylene, n-butene, n-pentene and higher alpha-olefins, which hitherto could only be polymerized to liquid dimers and trimers. These catalysts will also form polymers from olefins like ethylene, styrene, and butadiene, which have been polymerized by conventional means for

---

* Manager and Assistant Manager, respectively, Research and Development Division, Polymer Corporation Limited, Sarnia, Ontario.

many years. Secondly these catalysts form polymers which have structures having a high, and, in fact, an ultimate degree of orderliness, as opposed to polymers which contain a random distribution of isomeric units when prepared using conventional catalysts. The way has been opened to producing polymers with improved properties from cheaper raw materials.

Present Commercial Hydrocarbon Polymerization

Broadly speaking, in 1955 there were only three solid polyolefines manufactured in quantity (7), polyethylene plastic by the high pressure process evolved by Imperial Chemical Industries Limited, (175,000 tons/year in United states, 10,000 tons/year capacity in Canada), polystyrene plastic by bulk thermal or peroxy free-radical processes (225,000 tons/year, all types, in United States, 36,000 tons/year in Canada), and polyisobutylene or Vistanex (5,000 tons/year) by low-temperature ionic polymerization catalysed by boron trifluoride. Propylene, normal and isobutylenes, and higher olefins are converted to liquid dimers and trimers by passage over hot solid phosphoric acid catalysts, and used for polygasoline, detergent intermediaries and aviation gasoline components after hydrogenation. Isobutylene is polymerized to liquid polymers in solution using aluminum trichloride as catalyst.

The main classes of rubbery polymers in commercial production in 1956 contain the diolefins, butadiene and isoprene, and other hydrocarbons (8). These comprise general-purpose synthetic rubber (75 butadiene to 25 styrene, approximately 700,000 tons/year) and so-called high styrene resins (15 butadiene to 85 styrene, approximately 40,000 tons/year). Other combinations are possible, of course, using the peroxy initiated emulsion system, but have not found large-scale commercial application. A copolymer composed of 97% isobutylene and about 3% isoprene, Butyl (approximately 75,000 tons/year), is made in solution using aluminum trichloride as catalyst.

New Hydrocarbon Polymers

It is too early to predict what polymers made from these new catalysts will attain volume production, especially since all combinations of pairs of monomers have not been explored. Ethylene and styrene have been found to yield polyethylene (2,3,4,5) and polystyrene (3) with improved properties. Propylene, which hitherto could not be converted to solid polymers, gives materials which, depending on structure and molecular weight, give high tensile fibres, rigid molding resins or semi-elastic polymers (3,4,5). Butene-1, formerly not polymerizable to solid polymers by any means, gives rigid molding resins at least, and possibly other forms (3,5). It is possible moreover, to produce solid, plastic polymers from normal alpha-pentenes, hexenes, heptenes and octenes (3,5). Copolymers are possible, particularly such products as copolymers of ethylene with propylene or 1-butene. It is of interest to note that a minor modification of Ziegler catalyst makes it possible to prepare pure butene-1 from ethylene and pure 2-methyl-pentene-1 from propylene; such reactions (1) might be of interest for utilizing ethylene and propylene if surpluses exist having values only as fuel.

Many pure diolefin polymers have been reported. Five distinct varieties of polybutadiene have been prepared, all linear polymers differing in chain structure. There are cis-1,4, trans-1,4, syndoytactic-1,2, isotactic-1,2 and atactic-1,2 (3,9). A similar variety is possible from isoprene, but one, namely cis-1:4 polyisoprene, is of particular interest since it is the hydrocarbon known as natural rubber. The trans-1:4 (3,9) is similar to Balata. It is now possible therefore, to form solid polymers from the complete series of primary olefins and from the two simplest diolefins (2,3,4,5,9).

New Structures

To appreciate fully the scope and potential of these advances, we must consider the structures of these new polymers. All are based on the carbon atom, which, as shown in Figure 1, has four valency bonds, equally disposed, radiating in effect from the centre to the corners of a regular tetrahedron. This basic concept leads to the picture of carbon atom chains of zigzag or spiral form with the remaining bonds projecting forward and backward from the plane of the zigzag. In actual molecules the zigzag chain is coiled into a loose spiral. It also leads to a planar structure for a double bonded C=C group as shown. These are the basic concepts needed to account for the structures produced.

In Figure 2 we show the principal monolefins to be considered, all derivatives of ethylene. Polyethylene itself is composed of simple zigzag chains. Those of conventional polyethylene are formed by free radical growth in liquid ethylene; growing chains often attack chains already formed and result in branches, as depicted in Figure 3. The new polyethylene is formed by reactions in which few, if any, branches are formed, and the chains are therefore quite linear. As a result, the polymer chains can readily pack together and crystallize.

In Figure 4 is shown the structure of propylene. The unit, with the double bond opened, can have the methyl group in one of two positions, which we will call d and l. Polymers therefore could be all d form, all l form (which would be very similar), a regular alternation of d and l, or a random mixture, as shown in Figure 5. The pure d and l is called an isotactic structure, the dldl-form is called a syndyotactic structure, and the random chain is called an anisotactic or atactic. The first two are regular enough to crystallize and form rigid plastics, the atactic form is amorphous and rubbery. The higher olefins and styrene can be considered in exactly the same manner, except that the methyl group of

propylene is replaced by other groups as shown previously. The important practical point is that the three varieties of structure have been realized in pure form as linear chains using the new catalysts.

Turning now to the diolefins, in Figure 6 we see that butadiene and isoprene have very similar structures. Considering butadiene, one may consider turning it into a chain unit by opening both double bonds and then re-forming one pair leaving the other open to link with adjacent units as shown in Figure 7. This leads to a 1:4 unit or a 1:2 unit, depending on which pair is re-joined. The former exists in two forms, cis and trans, as shown, while the latter, by analogy with propylene, can take a d or an l form.

With these structures in mind we can now explain the structures of various polybutadienes, as summarized in Figure 8. Emulsion polybutadiene, to which ordinary synthetic rubber is related, is formed by free radical chain growth in an environment of butadiene. As a result, branched chains are formed as shown, and each chain contains a random distribution of all four units in unequal proportions. Commercial synthetic rubber contains fewer branches, a large proportion of the trans 1:4 structure, and also has styrene co-polymerized in the chain to confer processability and hardness; nevertheless it is still a random structure and will not crystallize. The pure structures are linear trans-1:4, cis-1:4, isotactic-1:2, syndyotactic-1:2 and atactic-1:2. All five forms have been synthesized in fairly pure state (3,9), although little is yet available on their properties. Among the corresponding isoprene structures, the pure cis-1:4 form and the pure trans-1:4 form are of interest, since these are the structures of natural rubber and Balata. Both of these forms have now been synthesized (3,9), as well as five of the remaining seven possibilities.

Nature of Catalysts

Apart from polyisobutylene and Butyl rubber, all present commercial

hydrocarbon solid polymers are formed by growing chains in an environment of pure monomer. The chains are initiated by free radicals, i.e. groups with an unpaired electron constituting a free valency bond, generated by decomposing such chemicals as peroxides and persulfates. As explained, the polymer structure tends to be branched with a random distribution of the various possible units in each chain.

The new catalysts are believed to consist of active surfaces which absorb monomers in specific fashion, and also open the double bonds. A monomer unit is believed to join an adjacent unit in a specific configuration, and the united unit to separate from the surface. The process of adsorption and polymerization continues at the surface and the polymer chain grows, rather like a hair from a follicle. No polymerization occurs in solution in this suggested mechanism, and so no random polymerization can occur. This picture is far from complete and is still mainly conjecture. These active surfaces can be prepared from a surprising variety of materials. The Ziegler catalysts for polyethylene(2) consist of complexes of aluminum triethyl and titanium tetrachloride, with many alternates possible for both metals. The Natta catalysts (3) for polyolefines and the Goodrich catalyst for polyisoprene (9) are of a similar type. The Phillips (5) and Standard Oil of Indiana (4) catalysts consist of silica or aluminum oxides impregnated with oxides of chromium, molybdenum, tungsten, uranium and others. It is likely that the methods of preparation are as important as the ingredients chosen. The reactions all take place at moderate temperatures, often below 100°C., and, rarely, below room temperature. The monomers must be free of oxygen and water, but can be and are used in solution in saturated hydrocarbons. Recently (10), it has been reported that modifications of the high pressure (Imperial Chemical Industries) process have been developed which permit production of polymers having properties similar in many respects to those made by

heterogeneous catalysis.

Properties of New Polymers

The outstanding property of linear isotactic polymers compared with random and branched polymers is tendency of the former to crystallize. As a result, linear polyethylene is harder and stronger than ordinary polyethylene(5). Isotactic polypropylene gives fibres stronger than nylon and ordinary polyethylene, and indeed approaches the tensile strength of steel (Table 1). The tendency to crystallize increases the density and the melting point (3) as shown in Table 2, and indicates the possibility that these materials may find use in piping, even in domestic hot water systems. Ordinary synthetic rubber requires carbon black to reinforce it before it will give high strength rubber stocks, as shown in Table 3. With cis-1:4 polyisoprene (9), the tendency to crystallize on stretching results in high strength even without stretching; the absence of styrene in this polymer makes for good rebound. Whether other copolymers, particularly from butadiene, will make superior rubbers remains to be seen.

Conclusion

In addition to the interesting properties of isotactic polymers, we must also remember that they have been made from inexpensive raw materials (12) of very low cost compared with the raw materials for Nylon and Dacron for instance (Table 4). In Tables 5 and 6 are listed the plants built or under construction already to make use of these new catalysts (13). It is estimated that over fifty million dollars per annum is now being spent on research in this field. When one considers that only hydrocarbons have so far been studied, with comparatively little attention yet directed to derivatives such as vinyl chloride, acrylonitrile or vinyl acetate, it is seen that a whole new complex of synthetic materials await discovery and application in the petrochemical industry.

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TABLE 1

PROPERTIES OF FIBRES (11)

Material	Ultimate Tensile Strength lbs./sq. in.	Tenacity gms. per Denier	Elongation Percent	gms./cc Density
Isotactic Polypropylene	110,000	9.3	31	0.92
Ordinary Polyethylene	23,000	2.0	50	0.92
Ordinary Nylon	75,000	5.2	29	1,14
Acetate Fibre	25,000	1.4	27	1.32
Steel	299,000	3.0	8	7.80

TABLE 2

PROPERTIES OF PLASTICS

	Density gms./cc	Melting Point ° F.	Tensile Strength lbs./sq. in.
Polyethylene			
Normal	0.91	239	2,060
New	0.96	247	4,500
Polypropylene			
Amorphous	0.85	167	Rubbery
Isotactic	0.92	320	5,000
Polystyrene			
Normal	1.04	230	(5,000)
Isotactic	1.08	446	(5,000-8,000)
Polybutene-1			
Amorphous	0.87	149	Rubbery
Isotactic	0.91	260	(2,000-3,000)

TABLE 3

PROPERTIES OF HYDROCARBON RUBBERS

Properties of Vulcanized Rubbers	Emulsion Polybutadiene		Bd/St 72/28 Copolymer		cis-1:4 Polyisoprene	
	A	B	A	B	A	B
Tensile Strength (lbs./sq. in.)	500	2,450	245	4,200	3,500	4,000
Elongation at Break %	350	270	525	675	850	600
Rebound at 77°F. %	69	59	74	63	86	71
Freeze Point °F.	-110	-110	-65	-65	-72	-72
Tread Wear	-	110	-	115	-	90

A - Gumstocks; B - Reinforced with Carbon Black

TABLE 4

MONOMER PRICES

Polymer	Raw Material	Price Cents/Pound
Polyethylene	Pure Ethylene	6 - 10
Polypropylene	Propylene-Propane	2 - 3
Polybutylene	Butylene-1	5
Polystyrene	Styrene	16
Polybutadiene	Butadiene	15
Nylon	Adipic Acid Ethylene Glycol	35 14
Terylene	Terephthalic Acid	35

TABLE 5

RIGID POLYETHYLENE PRODUCTION PLANS 1956 - 1957

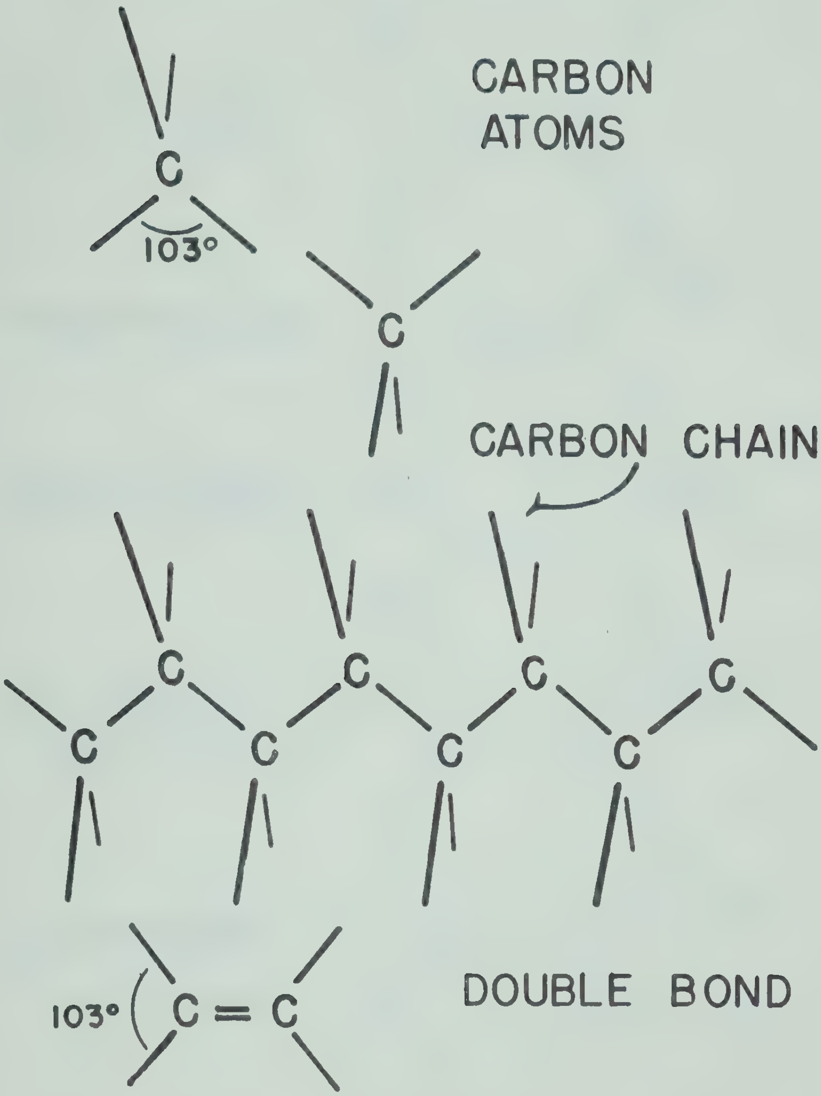
Company	Country	Production tons / yr.	Catalyst Type
Phillips Petroleum	U.S.A.	60,000	Phillips
Union Carbide	U.S.A.	30,000	Various
Koppers-Brea	U.S.A.	30,000	Ziegler
Koppers	U.S.A.	25,000	Ziegler
Celanese	U.S.A.	20,000	Phillips
Eastman, Spencer	U.S.A.		Standard
Monsanto, duPont, Shell			
Goodrich-Gulf, Hercules, Dow	U.S.A.		Ziegler
Kellogg, Grace	U.S.A.		Phillips
Farbwerke Hoechst	Germany	20,000	Ziegler
Rhein Chemie	Germany	20,000	Ziegler
Kohle-Oel Chemie	Germany	20,000	Ziegler
Rührchemie, Chemwerke Hüls, Hibernia, Rheinische Olefinwerke	Germany		Ziegler
Basische Anilin Soda Fabrique	Germany		Phillips
Dutch State Coal Mines	Holland		Ziegler
Union Carbide	England	10,000	Ziegler
British Hydrochemicals	England	10,000	Phillips
Shell, Monsanto	England		Ziegler
Pechiney	France	-	Ziegler
Rhone Poulenc	France	-	Phillips
Solvay	Italy	-	Phillips

TABLE 6

NEW POLYOLEFIN PRODUCTION PLANS 1956 - 1957

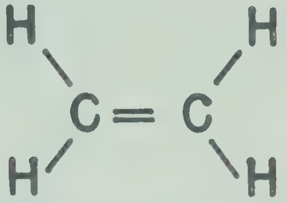
Polymer	Company	Country	Production
Polypropylene	Phillips Licencees	U.S.A.	Pilot
	Montecatini	Italy	Few tons/day
	Shell Chemical	England	Pilot
	Farbwerke Hoechst	Germany	Pilot
	Chemwerke Hüls	Germany	Pilot
	Hibernia	Germany	Pilot
Cis-1:4 Polyisoprene	Firestone	U.S.A.	Pilot
	Goodrich-Gulf	U.S.A.	Pilot

CARBON STRUCTURES

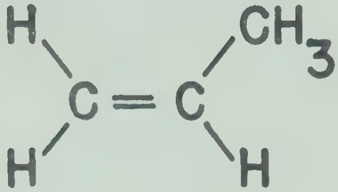


MONOLEFINS

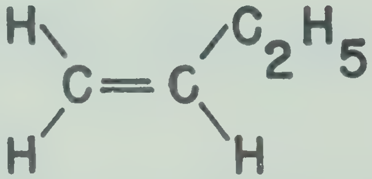
ETHYLENE



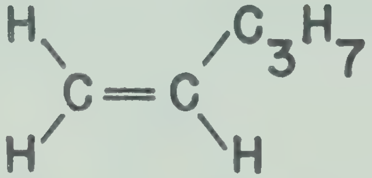
PROPYLENE



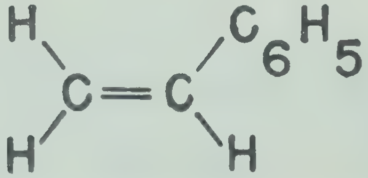
BUTYLENE-1



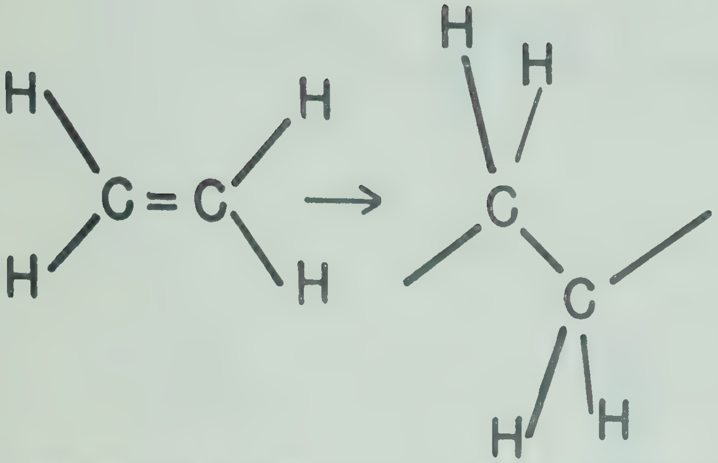
PENTENE -1



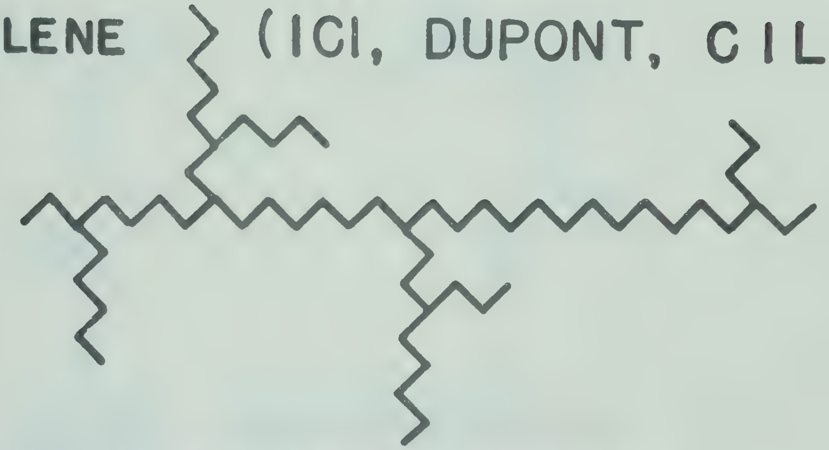
STYRENE



ETHYLENE

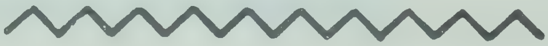


POLYETHYLENE (ICI, DUPONT, CIL)

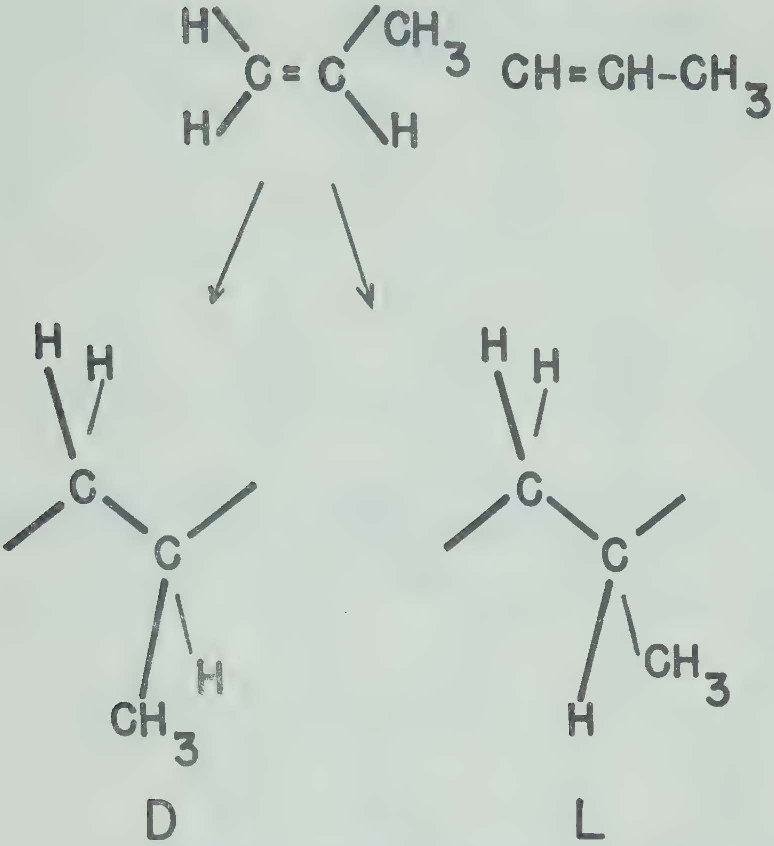


NEW POLYETHYLENE

(ZIEGLER, NATTA, PHILLIPS, S.O.I.)

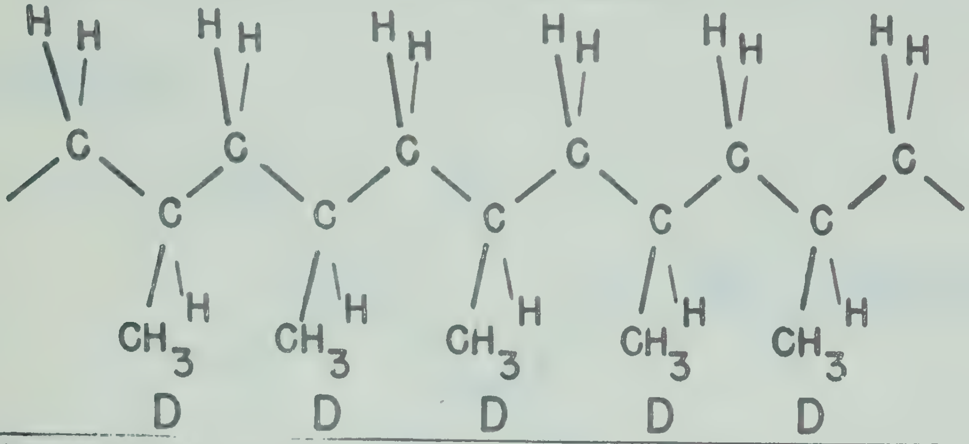


PROPYLENE

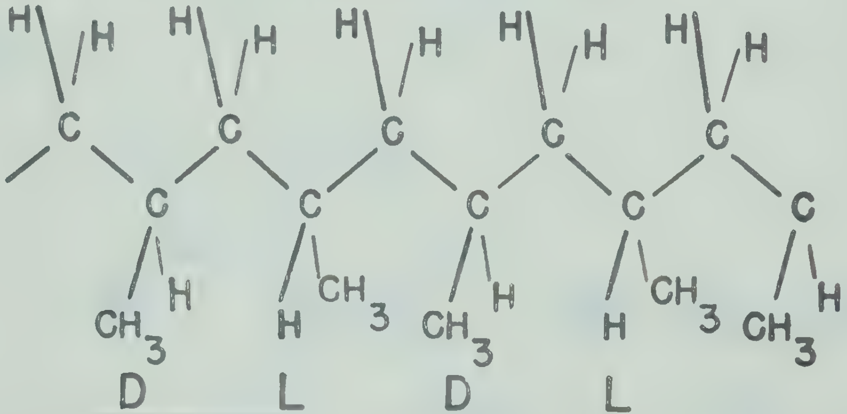


LINEAR POLYPROPYLENE
DDDDDDD or LLLLLLL
DLDLDLDLDL....
RANDOM DDLLLDLDDDDLL......

ISOTACTIC POLYPROPYLENE



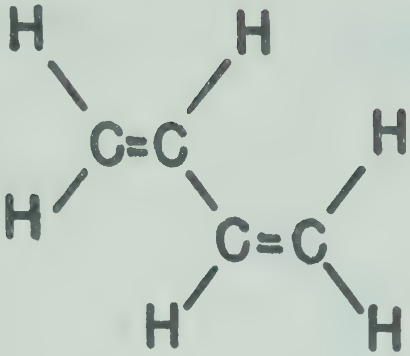
SYNDYOTACTIC POLYPROPYLENE



ANISOTACTIC OR ATACTIC

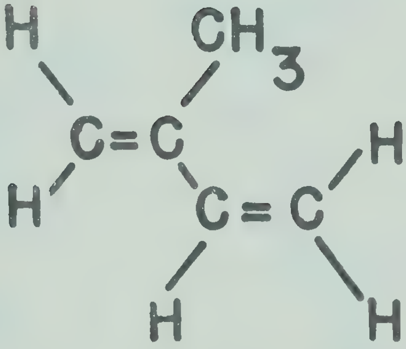
RANDOM D & L

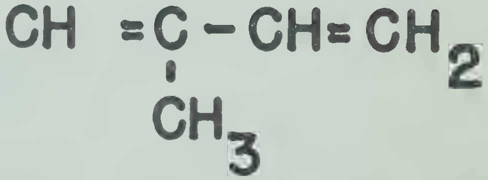
BUTADIENE



$CH_2=CH-CH=CH_2$

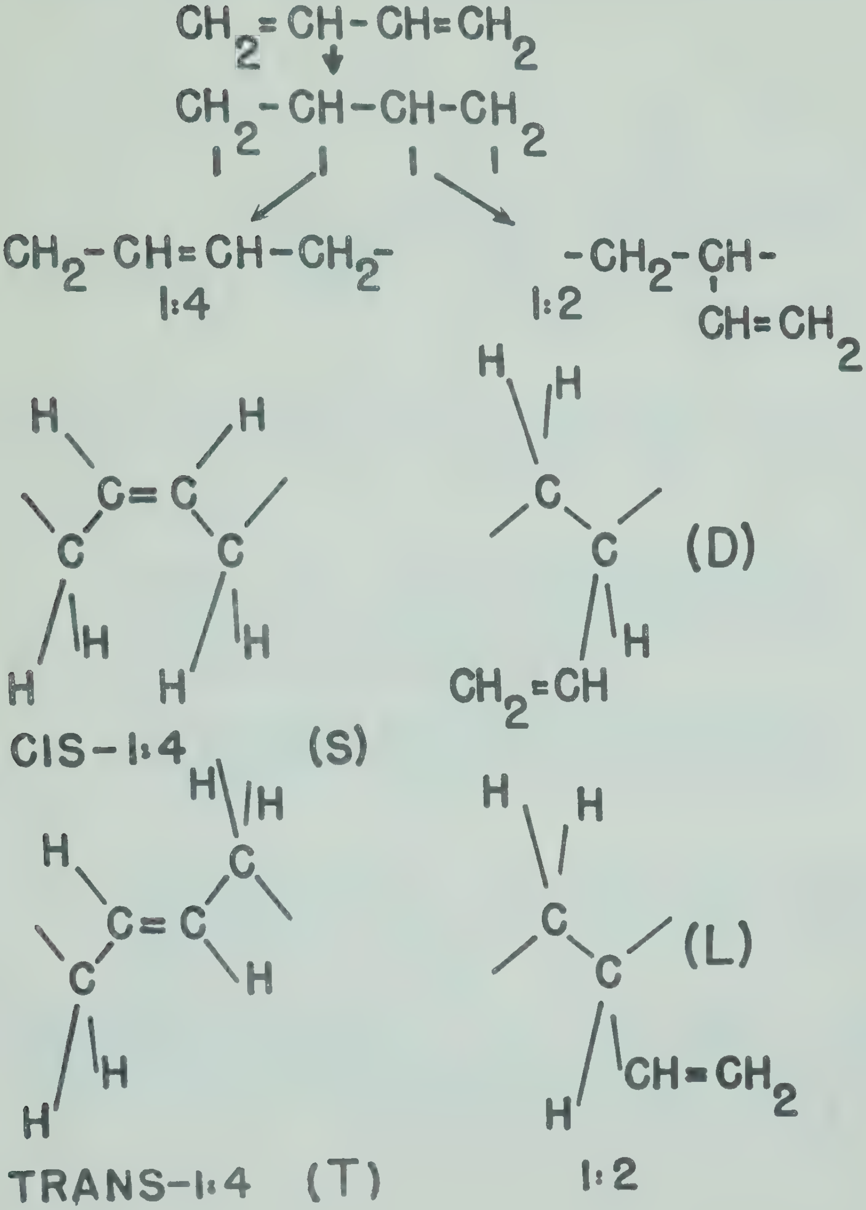
ISOPRENE





$$CH=\underset{\substack{|\\CH_3}}{C}-CH=CH_2$$

BUTADIENE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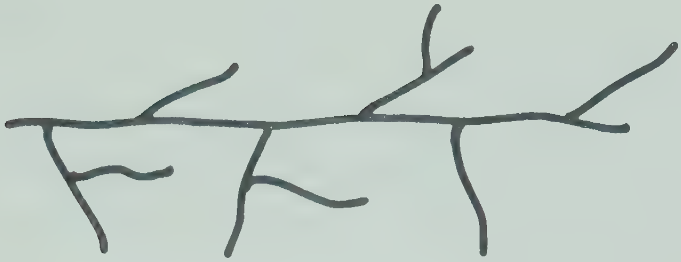
CH2-CH-CH-CH2
CH2-CH=CH-CH2-
1:4
-CH2-CH-
1:2
CH=CH2
H
C=C
C
CIS-1:4
(S)
(D)
CH2=CH
TRANS-1:4
(T)
(L)
CH=CH2
1:2

EMULSION POLYBUTADIENE



EACH BRANCH A RANDOM MIXTURE OF, S,T,D & L

CIS-1:4 POLYBUTADIENE

S S S S S S S S S

TRANS-1:4 POLYBUTADIENE

T T T T T T T

ISOTACTIC-1:2 POLYBUTADIENE

D D D D D D D....or L L L L L L L

SYNDYOTACTIC-1:2 POLYBUTADIENE

D L D L D L D L D L

DEVELOPMENTS IN THE CHEMICAL PROCESSING OF LIGHT HYDROCARBONS

by Edward C. Brown*

Light hydrocarbons — if one takes this expression to mean all the hydrocarbons containing up to, say, four carbon atoms — are the starting point of the manufacturing operations carried out by the petrochemical industry, and the reference in the title to "the chemical processing of light hydrocarbons" may suggest a review of developments that would cover the greater part of the petrochemical field. True, the title does exclude the production of aromatics from petroleum, most of the Oxo reaction products, sulphur and a few other petrochemicals, but it takes in a range of topics far too large to cover in a short review. This paper will therefore outline only briefly the role of the light hydrocarbons in the petrochemical industry, and then discuss in somewhat greater detail a few selected aspects of the chemical processing of light hydrocarbons.

Of the hydrocarbons containing up to four carbon atoms, those which find industrial uses as chemical raw materials include all the paraffins (methane, ethane, propane, normal and iso-butane), all the mono-olefins (ethylene, propylene, the normal butylenes and iso-butylene), one diolefin (1,3-butadiene) and acetylene.

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* Canadian Industries Limited, Montreal.

Two Main Routes From Light Hydrocarbons To Petrochemicals

For most petrochemical uses these light hydrocarbons are first produced from petroleum or natural gas as relatively pure individual chemicals which are then upgraded to more valuable commercial products by polymerization, by combination with other organic chemicals, or by reaction with oxygen, chlorine or other inorganic chemicals. Examples of this route to petrochemicals are: the separation of ethane which may be chlorinated to ethyl chloride; the manufacture of ethylene and its subsequent conversion to ethyl alchohol, ethylbenzene, ethylene oxide, ethylene dichloride or polythene; and the manufacture of acetylene from which acrylonitrile, vinyl chloride and a number of other derivatives can be made. These examples cover only the hydrocarbons containing two carbon atoms, but they are typical of a broad class of processes in which a new compound is built around the original structure of carbon atoms in the light hydrocarbon. The original light hydrocarbon structure is usually either retained or enlarged by the addition of more carbon atoms, but there are a few processes in which the number of carbon atoms may be reduced, as in the partial oxidation of C_3's and C_4's by Canadian Chemical Company at Edmonton to make formaldehyde, acetyldehyde, methanol and other oxygenated chemicals.

An entirely different route from light hydrocarbons to petrochemicals involves as the first step the conversion or reforming of the hydrocarbon to a mixture of carbon monoxide and hydrogen. This so-called synthesis gas is made by reacting either steam or oxygen, or both, with the hydrocarbon. The synthesis gas produced in this way,

usually from methane, is then used as a source of hydrogen (for example in the manufacture of ammonia), as a source of carbon monoxide for carbonylation reactions, or as the starting material for producing oxygenated chemicals such as methanol and the Fischer-Tropsch type of product.

There are therefore two general types of petrochemical manufacture based on light hydrocarbons, namely those in which the hydrocarbon serves as a nucleus or building block for new compounds and those involving conversion to synthesis gas. The remainder of this paper will review and discuss the primary processing steps in each of these routes to petrochemicals. First, it will deal with methods for producing and purifying the individual light hydrocarbons from which other petrochemicals may be derived, and then it will turn to methods for making synthesis gas.

Sources of Light Hydrocarbons

The light hydrocarbons utilized in the manufacture of petrochemicals may originate from three sources:

1. From natural gas. Some streams of natural gas, the so-called "dry" gas streams, consist of almost pure methane, but natural gas from many sources contains also ethane, propane, butanes and some higher hydrocarbons. Natural gas can thus be a direct source of all the paraffinic light hydrocarbons, but the manufacture of olefins or acetylene from natural gas requires hydrogen removal, usually achieved by cracking or pyrolysis.

As an example, ethane and/or propane, or even butane, from natural gas may be cracked or dehydrogenated to ethylene which is then purified as required for subsequent manufacture of other chemicals. This sequence of steps is performed in C-I-L's polythene plant at Edmonton, where ethylene is produced by cracking ethane separated from the residue gas, piped to Edmonton from the Devon absorption plant. In this case the ethylene is concentrated to 99.85% purity for polythene manufacture.

2. From petroleum refinery operations. Most of the operations carried out in oil refineries, from distillation of the crude oil through cracking, reforming, etc., give rise to "light ends" or gas streams containing light hydrocarbons, both saturated and olefinic. When these streams are processed to obtain maximum production of olefins rather than paraffins, it is customary to crack the latter, then recover and purify the total olefin product. Refinery gases are probably the commonest sources of olefins, and a number of examples of olefin production from refinery gas are found in Canada at the large refinery centers in Sarnia and Montreal East.
3. From the decomposition products of heavier hydrocarbons. When the desired light hydrocarbons are

not available from natural gas or petroleum refinery operations, which are normally the least expensive sources, they may be obtained by the deep cracking of crude oil or of selected liquid feedstocks produced in petroleum refineries. The objective in cracking processes of this type is usually to produce predominantly unsaturated light hydrocarbons, and it is characteristic of these processes that not one, but a wide range, of products is obtained. Imperial Oil's proposed petrochemical plant at Sarnia will crack liquid feedstocks to yield not only ethylene but also propylene, butylenes, butadiene, aromatics, etc.

In producing individual light hydrocarbons from any of these sources one or all of three processing steps may be involved.

1. Cracking or pyrolysis, which is usually required in the manufacture of olefins or acetylene but not for methane and its homologues;
2. Separation of the desired light hydrocarbon from the other hydrocarbons present in the source, or from the other hydrocarbons and hydrogen present in the gas mixture resulting from cracking;
3. Removal of contaminants such as sulphur compounds, carbon dioxide and moisture.

In the case of hydrocarbons with four or more carbon atoms, isomerization processes may also be involved, as in the conversion of normal butane to iso-butane.

Each of these aspects of light hydrocarbons production may be considered separately.

Cracking And Pyrolysis

Cracking may consist simply of hydrogen removal and the creation of double bonds, as in the production of ethylene from ethane or propylene from propane. It may also involve the breaking of carbon-carbon bonds, as in the production of ethylene from propane, butane, naphtha or gas oil. Finally, by using very high temperature conditions, followed by rapid quenching, it is also possible to form free radicals which will combine to produce acetylenic carbon-carbon bonds, as in the production of acetylene by the pyrolysis of methane.

In commercial practice the commonest form of cracking to produce olefins is to pass the feed hydrocarbon vapours through externally heated tubes or pipe coils, similar to the thermal cracking operations used in manufacturing gasoline from heavy petroleum fractions. Steam is frequently introduced with the feedstock to reduce carbon formation and lengthen the time between the burn-outs which are necessary to remove the carbon that builds up on the inside of the tubes. Operating pressures are usually relatively low, since the reaction involves an increase in gas volume and higher pressures lower the conversion. Temperatures of over 1500°F. are required to obtain good conversions of ethylene in a reasonable contact time. The breaking of carbon-carbon bonds takes place more easily and at a lower temperature than the dehydrogenation reaction, and therefore propane can be cracked to ethylene at a lower temperature than when starting with ethane.

In this type of cracking, conversions per pass of 50 to 70% are usual and overall yields of olefins can be increased by recycling unconverted feedstock. The yield of ethylene, before purification losses, is about 85% from ethane and 50% from propane.

Straight thermal cracking of this type can be used to produce light olefins from any of the three sources of light hydrocarbons previously mentioned — natural gas constituents, refinery gases, or liquid feedstocks. Catalysts are not normally used in cracking operations to give ethylene, but they are used where it is desirable to favor hydrogen removal and minimize the breaking of carbon-carbon bonds, as in the dehydrogenation of butanes to butylenes, and normal butylene to butadiene. In these instances the feed stream is preheated in a furnace to a temperature below the threshold for appreciable thermal cracking, and then passed through a chamber containing a catalyst which favors dehydrogenation. Steam is usually added to suppress undesirable side reactions. Another example of catalytic cracking to produce selectively a light hydrocarbon was the Super-suspensoid unit used by Polymer Corporation at Sarnia to make butylenes from gas oil.

The Kellogg process for producing olefins from liquid feedstocks provides an interesting variation from conventional methods of thermal cracking. In order to prevent carbon formation and other undesirable side reactions which may take place while the feedstock is being heated to cracking temperature, the heating period is reduced to a minimum by mixing the feedstock rapidly with highly superheated steam. This process was pioneered in the petrochemical plant of

Imperial Chemical Industries Limited at Wilton, England, where naphtha is cracked to give a mixture of olefins including ethylene, propylene, butylenes, and butadiene. In this plant the naphtha feedstock is preheated to only about 1100°F. and then mixed with enough superheated steam at 1850°F. to give the desired cracking temperature of 1700°F.

There are three other methods for ethylene manufacture which accomplish heating of the feedstock by some means other than by heat transfer through a metal surface as in a tube furnace. One of these is the pebble furnace, in which the feedstock is contacted with a moving bed of refractory pebbles which have been heated by fuel gas combustion in a separate unit. The cooled pebbles are recirculated from the reactor to the heater by bucket elevator or airlift and any carbon formed is burned off in the heater. This process has definite advantages in the cracking of liquid feedstocks, and two or three different units have been designed and are in operation in the United States. Another technique, which avoids the use of tube heaters, is the so-called autothermic cracking process in which the feedstock is mixed with air or oxygen in sufficient quantity so that partial combustion in a reactor will produce the desired cracking temperature. A process based on this technique has been proved on the pilot-plant scale for making ethylene from ethane or propane, but no commercial plants have been built on this continent. The third method involves regenerative heating, and will be discussed in more detail below.

The cracking processes reviewed thus far are intended to

produce olefins preferentially. Small amounts of acetylene are usually produced as well and frequently constitute an undesirable impurity which must be eliminated by selective hydrogenation. As mentioned previously, more severe conditions are required to produce significant yields of acetylene and it is also necessary to quench the reaction products rapidly to prevent the disappearance of the acetylene formed. The high temperature levels, of the order of 2200°F., which are necessary for acetylene production cannot be achieved in tubular furnaces so that it is necessary to devise other means of supplying the heat requirements for pyrolysis. Electric arc methods have been used with some success, but they are not economical under normal conditions because of their high power requirements. The pebble heater, previously described for ethylene production, will reach sufficiently high temperatures for acetylene formation but it is difficult to achieve rapid enough quenching in this equipment to keep the acetylene concentration at a useful level. Two other pyrolysis methods have been developed for acetylene production, one resembling the autothermic process for ethylene manufacture (part of the feedstock is burned to supply the process heat) and the other employing regenerative heating and cooling.

Of these two, the autothermic process, which is best known as the Sachsse process and is sometimes referred to as partial oxidation, is the only one which has been applied in a large commercial plant. In this process, oxygen and natural gas are separately preheated and introduced into a special burner in such proportions that part of the hydrocarbon oxidizes or burns to give temperatures high

enough to produce acetylene from the unburned portion of the natural gas. The burner gases are passed immediately to a water quench which lowers the temperature sufficiently rapidly to prevent the acetylene from decomposing to its elements. When starting from natural gas, yields of about 40% are obtained and the acetylene concentration in the product gas runs from about 8 to 9%. The acetylene is recovered by absorption in a solvent and the residue gas, rich in hydrogen and carbon monoxide, can be used as synthesis gas. The Sachsse process, originally developed by B.A.S.F. in Germany, is now used in several plants making acetylene from natural gas in the United States. Important advances in burner design, eliminating the need for refractories, have recently been made in Europe.

The regenerative furnace process, although not yet applied on a large commercial scale, is of considerable interest and is still under active development. Two forms of the furnace, the Wulff and the Koppers-Hasche, have been described in the literature. They are very similar and, in fact, both derive from the same pilot-plant research. The essential parts of the furnace are two regenerators made up of grooved ceramic tiles stacked in such a way as to provide a number of parallel passages for gas flow. These two regenerators are separated by a relatively small, empty reaction space. In operation, one of the regenerators (A) is heated to above the desired pyrolysis temperature by combustion gases obtained by adding fuel gas to the central reaction space and burning it with air entering through the other regenerator (B), which is warm from a previous cycle and acts as an

air preheater. When the desired temperature is reached, the combustion is stopped and the feedstock gas is passed through the hot regenerator (A). Pyrolysis takes place here and continues as the gas passes through the central reaction chamber, but when the gas reaches the other regenerator (B), which is now cold, the products are rapidly quenched. When the temperature of (A) falls too low for pyrolysis, the feedstock is shut off and regenerator (B) is reheated by another combustion cycle, with the air being preheated by entering through regenerator (A). Because of the cyclical nature of this process, it is necessary to have one or more pairs of furnaces to obtain continuous production. When operated on natural gas, the product composition is not unlike that from the Sachsse process, and acetylene recovery is again by solvent absorption. The acetylene content of the product gas runs up to 6% from methane or 13% from ethane or propane.

A small demonstration plant in California has used the Wulff process commercially for several years to make acetylene welding gas from propane but, although several engineering firms have offered to design and build full-scale plants, none has yet been erected. The published results indicate that the Wulff process should be economically competitive with the Sachsse process, and it has the advantage of not requiring investment in a tonnage oxygen plant. It can also be used on feedstocks other than natural gas (methane), and a recent development has been the adaptation of the process to produce olefins as well as, or instead of, acetylene. When methane is used as the feedstock it is not possible to produce high enough proportions of olefins to warrant their recovery, but when ethane is used conditions

can be varied to give product compositions running from 30% ethylene and 3% acetylene to 2% ethylene and 13% acetylene. It is thus possible to use the process to produce a gas mixture from which ethylene, or acetylene, or both, can be recovered. Similarly propane may be used to produce either or both of these gases, but some propylene is also produced which may be recovered as such or recycled for further pyrolysis. Some work has also been done on the production of ethylene and acetylene from gas oil and other liquid feedstocks. Developments along all of these lines are continuing and the results appear encouraging — someone may finally take the step of building a full-scale plant.

Separation And Purification Processes

The processes for separating and purifying light hydrocarbons are largely adaptations of distillation and absorption methods designed and highly developed by the petroleum refining industry. Because of the volatility of the light hydrocarbons, processing temperatures naturally tend to be lower and pressures higher than in customary refining operations. The separation of the saturated hydrocarbons and olefins originally took the form, in most installations, of a straight-forward, low-temperature distillation, involving fairly large refrigeration and compression loads. This was followed by a trend towards the use of oil absorption, using hydrocarbons in the pentane and gasoline boiling-point range as the solvent or absorbing oil to effect a concentration of a broad light-hydrocarbon cut from natural gas, refinery gas, or the product gas from a cracking furnace. After stripping the concentrated product from the absorption oil, fractional

distillation under pressure and at relatively low temperatures was still necessary to achieve the purities usually required, but there was an over-all economy over the use of low temperature distillation alone. Recent improvements in low temperature methods seem to be causing oil absorption processes to lose favor, but both may still have advantage in particular circumstances.

As mentioned previously, acetylene is recovered from pyrolysis processes by absorption in solvents, those most commonly used being dimethylformamide, butyrolactone, acetone and, in a recent modification, liquid ammonia. The recovery of olefins and acetylene from the same gas stream requires a substantially separate purification plant for each product, although some duplication of equipment can be avoided in the initial separation steps.

The Hypersorption process is a rather ingenious method of separating light hydrocarbons, involving the continuous counter-current adsorption of the individual components on a bed of activated carbon moving down a tower. Because of the differences in the tendency of the hydrocarbons to adsorb on the carbon, a fractionating effect is achieved. Steam is used to regenerate the carbon. This system has not found wide favor, however, and there is only one installation operating in Canada.

Finally, some concentration processes depend on chemical combination methods such as the reaction of olefins with sulphuric acid. Solutions of ammoniacal copper compounds form complexes with many olefins and have been used to remove them selectively from gas streams.

The removal of contaminants such as sulphur compounds, carbon dioxide and moisture from hydrocarbon gases has been highly developed. Conventional methods for sulphur and carbon dioxide removal employ alkaline scrubbing solutions such as the ethanolamines, potassium carbonate and caustic soda. Moisture may be removed by scrubbing the gases with diethylene glycol or by passing them over solid desiccants such as alumina.

Before leaving the subject of olefin and acetylene production, there is an important point to note in connection with the scale of operation necessary to achieve minimum manufacturing cost. The plants involved are characterized by high investment per unit of production, and must be built in large sizes to be economic and competitive. In ethylene manufacture, for example, 25 million pounds a year is about the smallest size that one would consider building, 50 to 100 million pounds a year can be produced at considerably lower cost, and maximum economy is reached at 200 million pounds or more a year. The reason for this lies in the nature of the separation and purification processes, in which the capital cost is usually concentrated in a number of towers whose size can be scaled up to very large throughput capacity with considerably less than a proportionate increase in cost. The actual production of dilute gas streams containing olefins or acetylene, whether it be in a tube furnace, catalytic reactor, Sachsse burner or Wulff furnace, can be carried out economically on a relatively small scale; the maximum practical furnace size is soon reached and multiple units are required for large installations. Yield and heat requirements, rather than unit investment, are likely to be the factors

influencing choice of a cracking process and the scale of operation is not too important. But in the purification of the gas coming from the cracker, unit investment is all-important and large size is essential to achieve low costs.

The Synthesis Gas Route

Up to this point the discussion has dealt with the processing steps involved in obtaining individual light hydrocarbons in sufficient purity for use in further chemical manufacturing operations. As mentioned previously, there is another important route to petrochemicals production, namely the synthesis gas route leading to ammonia, methanol and other oxygenated chemicals.

Prior to the petrochemical era, synthesis gas was prepared from coal or coke and steam by the well-known water gas reaction.

$$C + H_2O \longrightarrow CO + H_2$$

Further reaction with steam over a catalyst in the so-called shift reaction can be used to make additional hydrogen at the expense of all or part of the carbon monoxide.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Thus, any mixture from one-to-one $CO:H_2$ ratio to pure hydrogen can be obtained after scrubbing out the carbon dioxide. Maximum hydrogen production is desirable for ammonia manufacture, whereas various ratios of hydrogen to carbon monoxide are required for methanol and the Fischer-Tropsch and Oxo types of synthesis. The carbon monoxide content can be increased by adding carbon dioxide and, in effect, reversing the shift reaction.

Synthesis gas mixtures can be obtained also from saturated hydrocarbons by treatment with steam at high temperatures in the presence of a catalyst — the so-called steam reforming process. The reactor containing the catalyst is heated externally. Unsaturated hydrocarbons cannot be used because they poison the catalyst. Hydrocarbons give synthesis gas mixtures richer in hydrogen than those produced from coal, and the hydrogen content can be increased to 100% by using the shift reaction and subsequent purification. Because of its abundance and low cost, natural gas consisting largely of methane is the hydrocarbon source most commonly used in this process. Hydrogen was made from natural gas commercially early in the 1930's, but the first true production of synthesis gas from natural gas was introduced only in 1941. This was at the wartime ammonia plant of Alberta Nitrogen Products at Calgary. Because of its lower capital and operating costs, the steam reforming of natural gas was adopted in preference to processes based on coke in most of the many new ammonia and methanol plants built on this continent in the postwar period.

The success of the steam reforming process was followed by the development of the Texaco partial oxidation process which under certain circumstances may be more economic. In this process no catalyst and no external heat are needed other than some preheating of the feed gases. The hydrocarbon and a suitable proportion of oxygen are fed to a reactor resembling a furnace where the combustion of part of the hydrocarbon produces the temperature required for synthesis gas formation.

$$CH_4 + \frac{1}{2} O_2 \longrightarrow CO + 2H_2.$$

Steam may be admitted with the feed gases to assist in temperature control and increase the hydrogen concentration of the synthesis gas. For ammonia production, the gas from the reactor goes through a shift convertor to get maximum hydrogen production. The lower cost of the partial oxidation reactor compared to a steam reforming unit is offset by the necessity for an oxygen plant, but the partial oxidation process has the advantage that it can be operated at higher pressures — up to about 500 p.s.i. versus a maximum of about 150 p.s.i. for steam reforming. This means that the reactor can be kept to a smaller size for a given throughput, and also, where the feedstock is available under pressure, this pressure can be maintained with a consequent saving in compression costs in subsequent high pressure synthesis steps, such as ammonia or methanol manufacture. Catalytic partial oxidation processes which operate at lower temperatures have also been developed but have not found wide commercial application.

The partial oxidation process is also more flexible than steam reforming, in that heavier feedstocks all the way up to residual fuel oils may be used. Two ammonia plants based on the partial oxidation of fuel oil are now nearing start-up, one of which is being built by C-I-L near Kingston, Ontario. A full-scale experimental ammonia plant using the partial oxidation of powdered coal is also being operated in the United States; if it is successful, coal may resume an important role in synthesis gas production. Also, there is a trend towards the increasing use in ammonia manufacture of by-product hydrogen from petroleum reforming operations, and of hydrogen separated from coke-oven

gas. Thus natural gas is no longer supreme as the most suitable starting point for synthesis gas and hydrogen manufacture.

The steps involved in purifying synthesis gas vary according to the use for which it is intended. Carbon dioxide, sulphur compounds and moisture may be removed by conventional methods previously mentioned. Carbon monoxide removal, when pure hydrogen is desired for ammonia manufacture, is achieved either by absorption in ammoniacal copper solutions or by scrubbing with liquid nitrogen.

Review Of Partial Oxidation Processes

It may be of interest to refer back to several of the methods of processing light hydrocarbons that fall into the category of "partial oxidation". This term is used to describe a number of processes which have the common feature of starting from a mixture of a light hydrocarbon and oxygen, or air, but each of the so-called partial oxidation processes gives rise to quite different products. The use of the same term, "partial oxidation", to describe so many different processes may cause some confusion which can be clarified by looking at what these processes have in common and how they differ.

The partial oxidation processes derive their name because the amount of oxygen used is always considerably less than would be required to convert all the hydrocarbon to carbon dioxide and water. The differences between partial oxidation processes lie in the proportions of hydrocarbon and oxygen used, in the temperature and pressure conditions prevailing, and in some cases on the use of a catalyst. The amount of oxidation allowed to take place is important in determining the reaction

temperature as well as the nature of the products.

The mildest,partial-oxidation reaction conditions are employed in the production of aldehydes, alcohols, organic acids and acetone. In the Celanese process used by Canadian Chemical Company, for instance, C_3 and C_4 hydrocarbons are reacted with about 10 times the volume of air, and about 100 times the volume of steam, the reaction conditions being of the order of 700°F. and 400 p.s.i. The reactants are preheated and the heat evolved by oxidation is relatively small. The amount of oxidation is stopped at the desired point by quenching. There is some breaking of carbon-carbon bonds but little dehydrogenation, and the products are essentially oxygenated hydrocarbons.

In what has been referred to previously as the autothermic cracking of ethane to ethylene, preheat is also used and the heat produced by oxidizing or burning part of the ethane in air is allowed to raise the temperature to 1500 to 1600°F. This results in the formation of carbon monoxide and water from the combustion reaction, but at this temperature part of the ethane is cracked to ethylene and hydrogen.

If a somewhat larger proportion of oxygen is used and if the temperature is made to rise to about 2200°F., acetylene is formed, as well as carbon monoxide and hydrogen. In the Sachsse process, temperatures of 2800°F. or more are used, so that essentially flame conditions are achieved, the pressure being kept in the neighbourhood of atmospheric. To prevent the acetylene from decomposing into its elements, rapid quenching is necessary.

By using about the same proportion of oxygen and operating

for longer reaction times at 2000°F. or more, but below the temperature at which acetylene is formed, hydrocarbons can be almost entirely eliminated from the product, which becomes essentially carbon monoxide and hydrogen. This is the Texaco partial oxidation process for making synthesis gas. The same result can be achieved at lower temperatures by using catalysts, but this is a more expensive alternative and has not found wide commercial use.

One other partial oxidation process, which has not been referred to previously, is used to make epoxides by the addition of oxygen to olefins. This depends on the use of a preferential catalyst, such as silver, and finds wide commercial application in the manufacture of ethylene oxide from ethylene and air or oxygen.

There are other examples of the partial oxidation of hydrocarbons, such as the manufacture of phthalic anhydride from naphthalene or the oxidation of cyclohexane to cyclohexanol and cyclohexanone, but these do not fall within the field of light hydrocarbons.

This review of the chemical processing of light hydrocarbons has attempted to include enough of the fundamentals to provide a background and show the interrelationships of the various commercial processes so as to give some orientation to those who are not familiar with this basic part of the petrochemical industry. From this background the paper has gone on to discuss some of the new processes that are being adopted, and the trends that are appearing.

Finally it should be pointed out that many petrochemicals can be made from more than one starting material, not always of petroleum

[illegible]

[illegible] through growth [illegible]

[illegible], monetary [illegible]

[illegible]

origin. For example, vinyl chloride can be made from either ethylene or acetylene made from petroleum or natural gas, or from acetylene made from calcium carbide. There are now half a dozen starting points in use for ammonia manufacture. It has not been possible to discuss in detail these competitive aspects involved in the choice of raw materials and routes to petrochemicals, but the subject cannot be closed without drawing attention to their importance in determining the form which the petrochemical industry has taken in this country.

ECONOMICS OF THE PETROCHEMICAL INDUSTRY

by W. Dunnington*

The economic factors affecting the petrochemical industry in Western Canada have been reduced in this paper to two questions:

(1) Why build a chemical plant anywhere?

(2) Why build a chemical plant in Alberta?

The first question may be answered by examining return on investment. Pay-out calculations or other variations of the method also may be used. In any case the final economic hurdle is the question, "Will the venture make enough money so that someone will put up the required capital?" Return on investment can not only answer this question but also determine whether a plant should be constructed in the east or west.

Return on investment as shown in Chart No. 1 is determined by dividing net annual profits in dollars, by investment dollars. The resulting percentage is the number which will be referred to frequently as return.

Net profit is gross profit less taxes.

Gross profit is sales less cost of sales.

Cost of sales includes mill cost, which in turn includes raw materials, services, labor, depreciation, etc., plus freight and delivery costs, plus selling expenses, plus administrative expense.

Investment includes the cost of the plant proper, plus its share of necessary land and services, plus working capital.

Many economic and technical questions must be answered affirmatively before a company can proceed with facilities for manufacture of a chemical or petrochemical. There must be a market and preferably it should be a growing

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* Development Manager, DuPont Company of Canada Limited.

CHART I

$$\text{RETURN ON INVESTMENT} = \frac{\text{NET PROFIT}}{\text{INVESTMENT}}$$

NET PROFIT = GROSS PROFIT···TAXES

GROSS PROFIT = SALES···COST OF SALES

- COST OF SALES
  - MILL COST
    - Raw Materials
    - Services
    - Labour
    - Depreciation
    - Etc.
  - FREIGHT & DELIVERY
  - SELLING EXPENSE
  - ADMINISTRATIVE EXPENSE
- INVESTMENT
  - MANUFACTURING PLANT
  - LAND & SERVICES
  - WORKING CAPITAL

market — even after allowance has been made for the inroads of competitive products. The required technology must be available — not only that required to build and start the plant, but a continuing, ever-improving technology based only upon a sound technical foundation and continuing research and development effort.

The economic factors can normally be related to return on investment. Plant size, or more precisely sales volume, is usually the most critical element in the economics of a petrochemical venture.

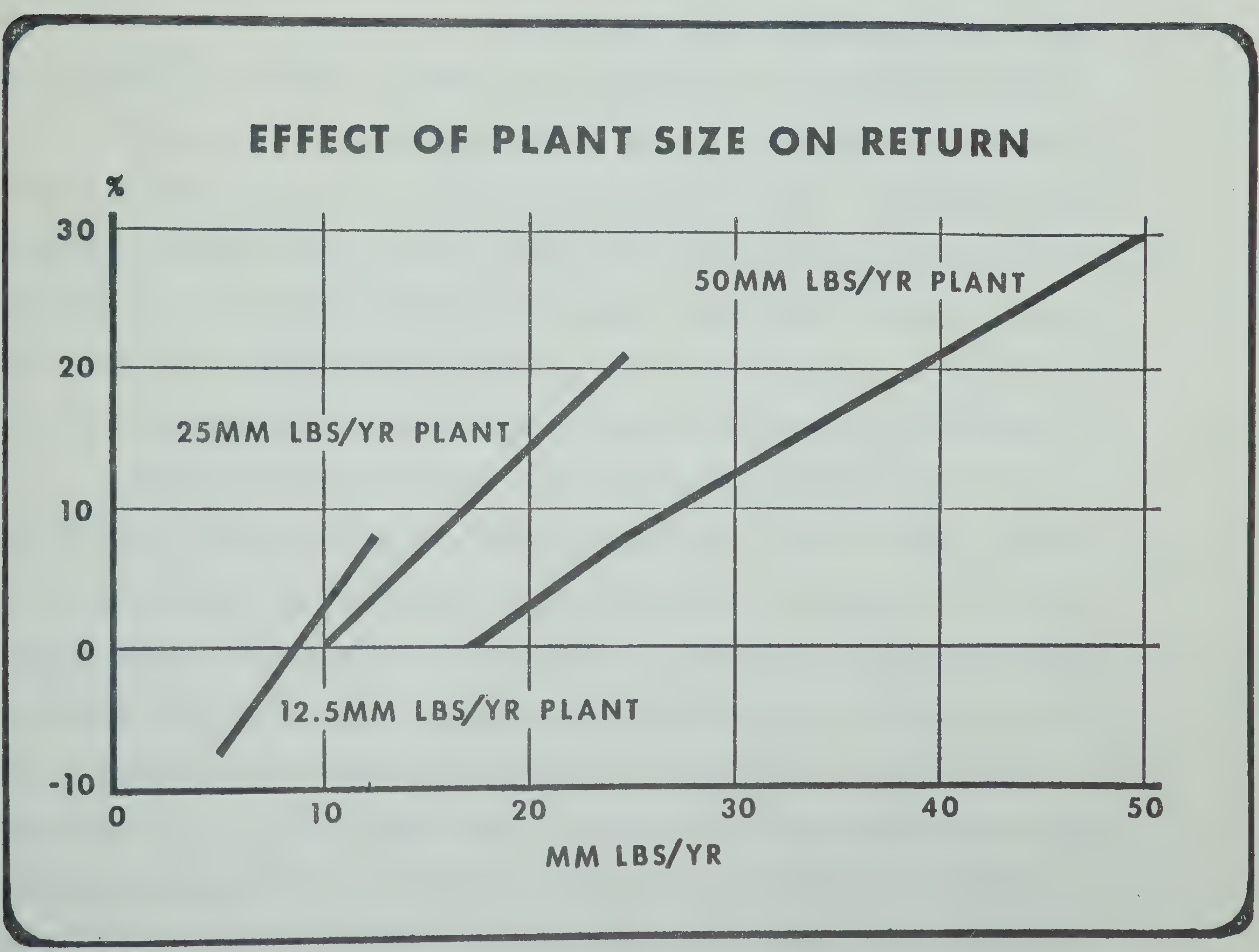
The curves on Chart No. 2 are plotted for a hydrocarbon-based product, showing the returns, which could be made by 12½, 25 and 50 million lb./yr. plants, versus sales volume in millions of lbs./yr.

It is evident that the larger the plant the greater the return when the comparison is made at full capacity. As plant size is increased, the advantage diminishes. By doubling the 12½ million lb./yr. plant, the return at full capacity will increase from 8% to 21%, or 160%. Doubling the 25 million lb./yr. plant would increase return from 21% to 30%, or about 40%. A 100 million lb./yr. unit would earn a higher return than two 50's but the improvement would be less spectacular.

Theoretically there is an upper limit of size where further increases will not increase returns, and this is often assumed to be at the point where the largest individual pieces of apparatus which can be constructed are in use, but there is some doubt that this is a point rather than a plateau. Usually the reason for a second unit is found in lower freight to markets or some factor equally unrelated to plant size per se.

It is clear also that once having constructed a plant it is most desirable to operate it at capacity.

CHART II


EFFECT OF PLANT SIZE ON RETURN
%
30
20
10
0
-10
0
10
20
30
40
50
MM LBS/YR
50MM LBS/YR PLANT
25MM LBS/YR PLANT
12.5MM LBS/YR PLANT

In the case of the product which is considered on this chart, the present Canadian market is about 5 million lbs./yr. or below the break-even point for the smallest of the three plants.

Examination of the market, however, indicates a rapid growth — which currently is typical in Canada. Forecasts indicate that the market will grow to 10 million lbs. in 1960 and 25 million lbs. in 1965. The $12\frac{1}{2}$ million lb. plant would make money for only a year or so before requiring major expansion. In addition the break-even point is not much better than the break-even point for a 25 million lb. plant; viz., 9 million lbs. versus 10 million lbs. Thus the 25 million lb. plant is probably the minimum size which should be built.

The product is being imported, in this case from the U.S. and sold at the U.S. price plus duty. The anti-dump law which applies to products manufactured in Canada states that the product of a foreign country cannot be sold in Canada at a price lower than the fair market value in the country of origin plus duty. The desirability of such a law, if we wish industry to construct plants here at the earliest possible date, is illustrated well by this chart.

By 1962, Canadian consumption will be about 15 million lbs. and at this volume a 25 million lbs./yr. Canadian plant would earn 8% return. With no import restrictions the Canadian plant could not expect to capture the entire Canadian market. If it could get only half the market (or $7\frac{1}{2}$ million lbs./yr.) the return would be below the break-even point and the plant would not be built. With an effective anti-dump law it is merely necessary for a Canadian manufacturer to drop the price below the laid down price of imported material to be permitted to supply the entire Canadian market. In the case of our example, Canada would get a new plant 2 or 3 years sooner as a result of a good anti-

dump law. It should be noted that the forces of competition are still at work. Even though there is only one plant in Canada prices must be maintained below prices of imports.

It may be seen also that when a plant is expanded there is a decrease in return on investment for a period but that eventually the return becomes higher than had been the case for the smaller unit.

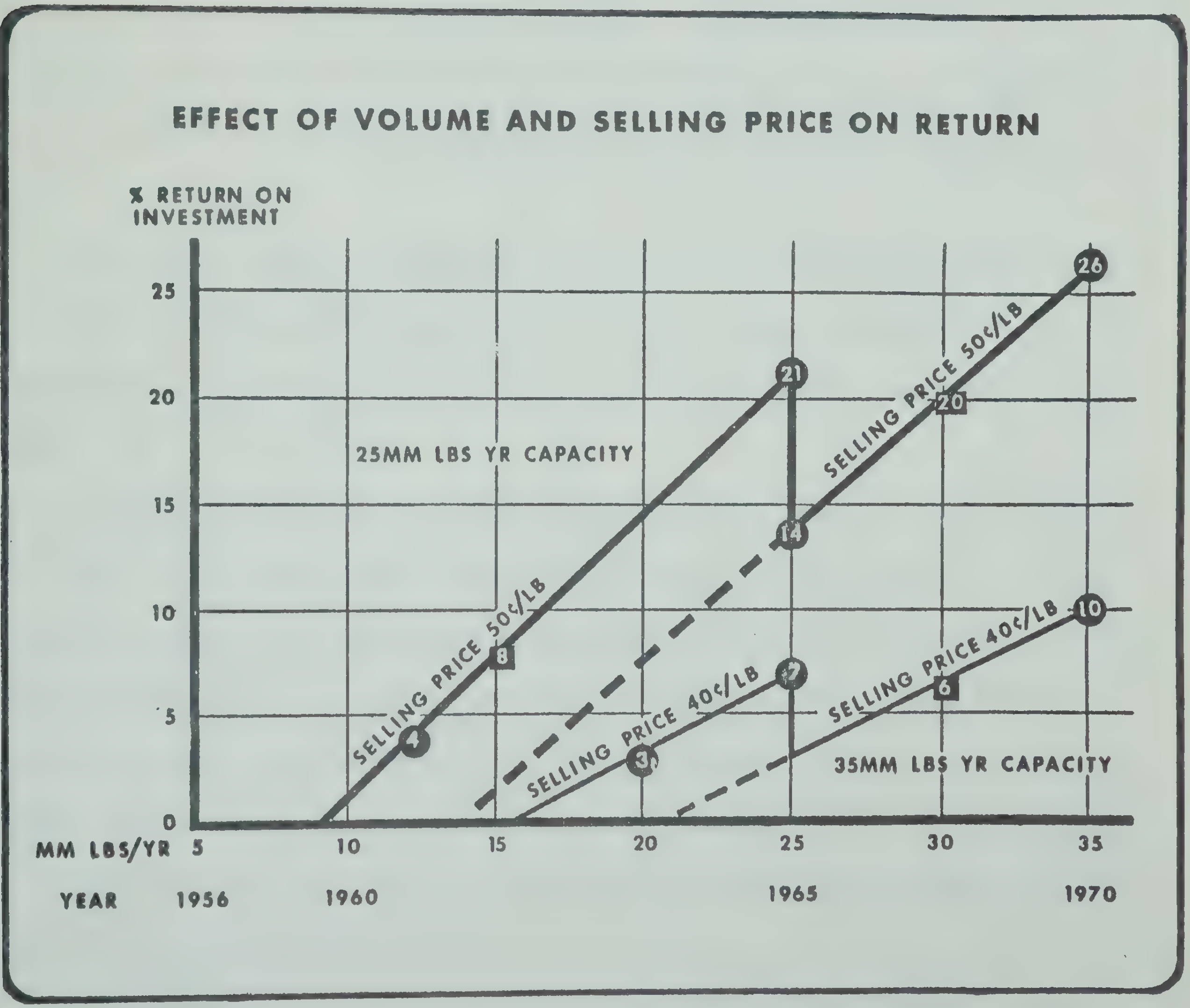
Further examination of the future of the 25 million lb. plant indicates that at present selling prices it would earn about 21% return at full capacity.

This might tempt a second manufacturer to enter the business and introduces one of the more important concepts of the economics of competition in the Canadian chemical industry. Competition has come to mean two or more plants manufacturing the same product and as a result offering the product to customers at lower prices than would be the case if one of them had a monopoly. In Canada the threat of a second manufacturer going into a business is far more likely to produce lower chemical prices than is the actual construction of a second plant. This generalization is likely to be true for any organic chemical during the early years following its initial manufacture.

Chart No. 3 shows return versus sales for the 25 million lb. plant extended to show the effect of expansion to a capacity of 35 million lbs. after sales reach the 25 million lb. level. In addition to the curve at the selling price of 50¢ a pound as indicated on the previous chart, a second curve has been added based on a selling price of 40¢ a pound.

Assume that manufacturer'A' has a plant in operation and that manufacturer 'B' has the required technology and could, if he constructed a plant and sold product at the same price as 'A', obtain half the market.

CHART III


EFFECT OF VOLUME AND SELLING PRICE ON RETURN
% RETURN ON INVESTMENT
25
20
15
10
5
0
MM LBS/YR 5 10 15 20 25 30 35
YEAR 1956 1960 1965 1970
25MM LBS YR CAPACITY
35MM LBS YR CAPACITY
SELLING PRICE 50¢/LB
SELLING PRICE 50¢/LB
SELLING PRICE 40¢/LB
SELLING PRICE 40¢/LB
4
8
21
14
20
26
3
7
6
10

'A' must consider before expanding his business and certainly before setting his selling prices whether 'B' has sufficient incentive to construct a plant. For example, when the market reaches 25 million lbs./yr., 'A' would normally expand his plant — in this example at a cost of several million dollars. This would decrease his return from 21% to 14%, but he would expect to recover his position as the market increased. However, should manufacturer 'B' decide to enter the field at this time, 'A's sales would drop to 12½ million lbs./yr. and his return would drop below the break-even point if he had increased his plant capacity to 35 million lbs./yr. 'B' could earn 4%. 'A' would probably then raise his price and 'B' would probably follow. Competition for markets would be on the basis of quality, service and other factors but not price.

The 40¢/lb. curve illustrates 'A's position if he drops his price before 'B' constructs a second plant. At the lower price, the return for a second manufacturer who captured half the market would be well below the break-even point.

An examination of the situation when the market reaches the 30 million lb. level will reveal that at 50¢ a pound and with the entire market, 'A' earns 20% on his investment. If 'B' manufactures and captures half the market,he will earn 8% and 'A's return will drop to less than 2%. Now had 'A' dropped the selling price to 40¢ a pound before 'B' built the second unit, his return would have dropped to 6%. However, it would then be impossible for 'B' to break-even.

The 10¢ price reduction is probably more drastic than would actually occur, but it illustrates the point.

At the 35 million lb. level the 10¢ reduction might be about right. The 50¢ price would allow 'B' to earn 11% if he could capture half the market. However, at 40¢ he would only make about 1%. 'A's return at half the market is

about 5%. By voluntarily dropping his price 20% and his return from 26% to 10%, it is probable that he will have retained the entire market. His sales of 35 million lbs. at 40¢ would be $14,000,000 instead of about $9,000,000 per year which he would obtain from 17.5 million lbs. at 50¢. The consumers will be better off by 10¢ a pound (or $3,500,000).

The important point is that with markets of the size we now have in Canada, a plant supplying the entire market will be able to reduce prices to consumers. Under the threat of competition it will do just this. After a second plant is built this incentive and perhaps even the ability to reduce prices will be gone.

It is of interest that the 20% price drop assumed in the example is well in excess of the duty for the product involved, which is another way of saying that a tariff which permits a Canadian manufacturer to supply the entire Canadian market will not necessarily be passed on to the customer forever, but may well be the means by which prices in Canada can be lowered.

Assuming that size and other problems have been solved and that a new petrochemical plant is to be built in Canada, should it be built in the West or in the East?

If the decision is to be made by private interests an analysis which determines the return at several potential locations will provide the answer.

In the case of the product considered in the previous curves, the market is in Eastern Canada but the major raw materials originate in the West.

A saving of 10% in raw material costs can be forecast if the plant is located in Alberta. The saving is greater for the major raw material but there are several minor ingredients which carry severe freight penalties, resulting in an average saving of 10% in raw materials. This increases return

CHART IV

EFFECT OF ALBERTA LOCATION ON RETURN

(percentage points)

	PLANT CAPACITY MILLION LBS/YR	
	25	50
10% SAVING IN RAW MATERIAL COST	1.6	2.2
10% INVESTMENT PENALTY	-2.0	-2.6
2¼¢ LB FREIGHT PENALTY	-3.3	-4.5
NET DECREASE IN RETURN	-3.7	-4.9

1.6 percentage points for the 25 million plant and 2.2 points for the 50 million plant.

Construction costs are expected to be higher in Alberta than in the alternative eastern location because of:

(1) Additional freight on construction materials,

(2) Higher labour rates,

(3) More severe climatic conditions.

Working capital is somewhat higher because of additional inventory required due to longer delivery time. A 10% increase in investment results in a decrease of 2.0 and 2.6 percentage points in returns on the 25 and 50 million plants respectively.

Then there is the usual 2½¢/lb. penalty on finished product shipping cost which reduces return 3.3% and 4.5% for the two plants.

The net advantage of the eastern location turns out to be 3.7% and 4.9% for the 25 and 50 million plants respectively.

Studies have indicated that this comparison is typical of many potential petrochemical operations.

Generally speaking the most important economic factors in alternate plant locations which can be reduced to dollars and compared easily are freight costs. In the case of petrochemical manufacture, possibilities of alternate feed streams such as natural gas, refinery off-gas, etc. may complicate the picture, but even here a freight analysis is likely to provide the answer to the fundamentally correct manufacturing location.

The price at which Alberta hydrocarbons can be sold is determined by competition. Natural gas can be sold in Eastern Canada at a price determined by the value of other fuels. Therefore the price which it will bring at the

Alberta border is the price in Eastern Canada less transportation costs. The same situation exists with relation to crude oil. The price which may be charged in Alberta is determined by the price at which off-shore crude can be delivered to Eastern Canada less pipeline transportation costs. Now any petrochemical manufacturer, other things being equal, will locate his plant at a point where his costs are least. At first glance therefore, since it has just been established that the hydrocarbon price in Alberta will be less than in Sarnia or Toronto by the transportation costs, it might be expected that all plants would be built in Alberta. This is not the case, however, because finished product must be shipped by rail, whereas raw materials may now be moved by pipeline. The cost of shipping a barrel of crude to Sarnia is about 65¢ as compared to a tank car rate of about $6.50.

It appears likely that most petrochemical ventures in Alberta will involve a net freight penalty. This will not always be true and some of the conditions which could result in a favorable freight picture for Alberta are set forth in Chart No. 5.

Obviously if markets are located in Western Canada or if markets can be most economically reached from west coast ports, Alberta would enjoy a freight advantage rather than disadvantage in finished product shipping costs.

In some operations the consumption of hydrocarbon raw materials and fuel may be large in comparison with the quantity of finished product shipped. In such cases savings in raw material shipping costs might well outweigh penalties in finished product shipping costs.

A third condition which would favor manufacture of a petrochemical in Alberta or at least eliminate any freight penalty would exist if finished product volumes were large enough to justify delivery by pipeline.

CHART V

CONDITIONS WHICH FAVOUR MANUFACTURE IN ALBERTA

(1) Markets in western Canada or export markets most economically reached from west coast ports.

(2) Consumption of a large quantity of hydrocarbon raw materials per pound of finished product.

(3) Finished product volume large enough to justify pipeline delivery.

(4) Special situation where raw materials are available as by-products of existing operations.

Finally there are and will be special situations where by-products from refinery and petrochemical operations will be available and where it will be profitable to sell such by-products (as ethane, propane and butane) at prices low enough to compensate for any finished product freight penalty. It is probably for such reasons that C-I-L and Canadian Chemicals have constructed their large petrochemical operations here.

When is construction of a petrochemical plant economically right or wrong from a provincial or national point of view? No attempt has been made to establish rules on this subject because the interests of a manufacturer or the province or the country as a whole may appear quite different, particularly on a short term basis.

For example, Alberta may be better off if a petrochemical plant is built within her borders. Ontario also might benefit if the same plant were built there. Location theory from the standpoint of theoretical economics would require consideration of many factors and much information which has not been considered here. Probably it would be possible to use the techniques of Operations Research and the calculating capacity of a Univac to determine new plant location and timing which would make the maximum contribution to the average Canadian standard of living.

Fortunately, in the absence of such elaborate studies, private enterprise appears to be able to select locations in the best interests of the greatest number of people by relying on return on investment analyses.

ECONOMIC AND OTHER FACTORS AFFECTING PETROCHEMICAL DEVELOPMENT IN WESTERN CANADA

by Donald Quon* and John Gregory*

The previous author, Mr. Dunnington, has made a substantial contribution to this discussion, particularly in his reaffirmation of the belief of industry that, from the view point of the country as a whole, the laws of economic return form the only sound basis for plant location. It is a valuable and perhaps necessary reminder to this audience because there may be a tendency for us in Alberta to become parochial in our thinking and to equate Alberta's interests with the national interests. That, of course, is not necessarily true, and it is clear that petrochemical development in Alberta, or Western Canada, will occur, not because we want it, or because we try to will it, but only when such development will most economically satisfy a particular demand.

This paper proposes to elaborate on and assess, perhaps in a little different way, some of the factors affecting petrochemical development that have already been mentioned.

Raw Materials

One important factor having a direct bearing on the future of the petrochemical industry in Western Canada was discussed earlier

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* Research Council of Alberta, Edmonton.

by Dr. Govier in this symposium — and that is the question of availability of hydrocarbon raw materials. In view of the immense quantities of natural gas that are to be used as fuel, and in view of the relatively small amounts required by even a very large petrochemical industry, it seems safe to conclude that the supply of natural gas hydrocarbons will certainly not be a limiting factor in the development of a petrochemical industry in Western Canada. Indeed, there may be a surplus of butane, and possibly propane, which might prove particularly attractive for petrochemical manufacturers.

Markets

The question of future petrochemical markets obviously has an important place in this discussion. It is true that forecasts of markets have to be used with discretion; however, they are useful in indicating, qualitatively at least, the trends that might be expected. A number of forecasts have been made recently — in the United States by the President's Materials Policy Commission, more popularly known as the Paley Commission; and in Canada, in various submissions to the Gordon Commission. Only a very few general and brief conclusions can be listed here:

1. As raw materials for the synthetic organic industry, petroleum and natural gas hydrocarbons are in a unique and almost unrivalled position. They are likely to remain so.

2. The over-all future of the petrochemical industry seems very bright. The American petrochemical industry has doubled every five years in the last decade and a half — showing an annual growth rate of 14% as compared to 10% for the entire chemical industry and 3.0% for over-all industrial production. It is expected to double again between 1955 and 1960. In 25 years the petrochemical industry in America should be 4 or 5 times as large as at present — and indeed, this prediction may be rather conservative. There is no need to belabor this point further. It may be said with assurance that there will be a very substantial expansion of petrochemical markets in the coming years. The question is — in what part of the country is it most likely to develop?

3. The petrochemical industry will continue to evolve and undergo many changes. Rapid technological obsolescence will be a standard operating hazard. There will be shifts in the raw material sources for synthetic organic chemicals — some from petroleum and natural gas hydrocarbons to alternative sources like coal, and vice versa, but probably even greater shifts will occur between various fractions in the petroleum family — some recent examples being the shift from natural gas to petroleum fractions as a feedstock for making carbon black, and another, the shift from refinery off-gases to high ethane natural gases as primary sources of ethylene. All these shifts will, of course, influence markedly regional petrochemical development.

In the ultimate technical sense, because of the many advanced techniques developed in handling hydrocarbons — covering such processes as decomposition, polymerization, hydrogenation, dehydrogenation, cyclization, aromatization — the different hydrocarbon sources are practically interchangeable.

4. The matter of tariffs is an important consideration in studies of petrochemical development in Canada, and in recent years this subject has been given much attention. There are two aspects to this question, firstly, that of tariffs imposed by other countries on goods manufactured in Canada and secondly, that of Canadian tariffs imposed on chemicals entering Canada. In practice, the Canadian manufacturer has, in effect, little or no entrance to the American market and this situation is not likely to change. An export market can develop, however, and indeed already has been developed in the rest of the Commonwealth, in Europe, and may in time be extended to the Far East.

On the question of tariffs on organic chemicals coming into Canada the matter is complicated by the fact that the products of one industry may be the raw materials of another. In Canada, where the petrochemical industry is in early stages of development, some firms must import chemical intermediates from the United States and for their survival must obtain these imports duty free. Even within single companies there are mixed feelings as to the extent they may wish to press for tariff protection for the chemical industry.

The petroleum industry in Western Canada is based on hydrocarbon raw materials and produces either finished products or intermediates. It does not utilize intermediates to any large degree and therefore the tariff inequalities on chemical products are of even more concern to the industry in Western Canada than in the country as a whole.

Primary Location Factors

The main source of hydrocarbons in Canada is in the West, and primarily in Alberta. True a considerable tonnage of crude oil is still imported into Eastern Canada but this will not affect the main argument.

In such a situation, the primary location factors for a petrochemical industry are:

1. Transportation costs of raw materials and fuel gas;
2. Transportation costs on finished products;
3. Economies and diseconomies of scale.

This analysis is based on the premise that plant costs, interest and related charges, maintenance costs, cooling water costs, and most chemical costs probably do not vary too significantly between regions, and that the costs of labor and power, which are normally required in relatively small amounts, are not important location factors. Differences in fuel, steam, and feedstock costs are therefore due to transportation costs.

Since the previous paper has covered the third factor in some detail, the present discussion will be limited to the other two factors.

The comparative transportation costs for the different hydrocarbon feedstocks are shown in Table I.

TABLE I

HYDROCARBON RAW MATERIAL TRANSPORTATION

Product	Costs by Pipeline ¢/lb./100 miles	Remarks
Methane	0.040	Estimated costs of 30-34 inch Trans-Canada Pipe Line.
Ethane	0.06?	Difficult to assess because normally transported together with methane.
LPG(propane, butane)	0.07 - 0.10*	Rough estimates for 8-12 inch pipeline based on U.S.A. experience.
Crude Oil	0.015	Established figure for existing large pipelines.

*LPG transportation costs are approximately 0.20¢/lb./100 miles by truck and 0.10 - 0.12¢/lb./100 miles by railroad tanker.

Some observations can be made from the above table:

1. Pipeline transportation of materials is relatively cheap. This fact will be brought out more clearly in a later section where cost figures for rail transportation are presented.

2. Relatively, crude oil is inexpensive to transport, propane and butane expensive to transport. High methane natural gas occupies an intermediate position.

The price structure of the different hydrocarbons at various locations in Canada provides an interesting sidelight, although it has only an indirect bearing on the main argument.

TABLE II
HYDROCARBON RAW MATERIAL COSTS AT VARIOUS LOCATIONS
¢/lb.*

	Edmonton*	Vancouver	Winnipeg	Toronto
Methane	0.30	0.55	0.60	1.10
Ethane	1.0?	1.4?	1.5?	2.2?
Propane	1.0	1.5	1.6	2.6**
Butane	0.7	1.2	1.3	2.3**
Pentane	1.5			
Crude Oil	0.9	1.0	1.0	1.1

* These costs are based upon a source price of 13-14¢ per MCF for natural gas, an estimated 1¢ per pound for ethane, 5-5½¢ per gallon for propane, 3½-4¢ per gallon for butane, 10-12¢ per gallon for pentane and $2.60 per barrel for crude oil. Transportation costs are based on figures shown in Table I.

** May be obtained from local refineries for perhaps 10-20% less.

Perhaps the most striking feature of this table is the fact that in Alberta, on a per pound basis, crude oil is three times as costly as natural gas but in Toronto the price is almost identical. The high value of liquefied petroleum gases, propane and butane, should also be noted.

Some typical rail transportation costs of finished products are shown in Table III.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

> [illegible]

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[illegible]

[illegible]

TABLE III

TYPICAL FINISHED PRODUCT FREIGHT COSTS

¢/lb./100 miles

Edmonton to	Vancouver	Winnipeg	Toronto
Fertilizer	0.09	0.09	0.05
Polythene (bags)	0.16		0.15
Formaldehyde	0.10		0.09
Propane	0.17	0.15	

It is evident that unit transportation costs of finished products by rail are much higher than transportation costs of hydrocarbons by pipeline — the cost being up to twice as much as for LPG's, three or four times as much as for natural gas, and up to ten times as much as for crude oil.

The key location factor is the amount of raw materials and fuel required to produce a unit weight of finished product. If this ratio is large, the industry will be raw-material-oriented; if it is small, it will be market-oriented. The cross-over point will depend upon the nature of both the hydrocarbon raw material and the finished product.

Some of the main petrochemical processes are outlined in Table IV.

[illegible]

[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]
[illegible]		[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

TABLE IV

PETROCHEMICAL RAW MATERIALS, INTERMEDIATES, AND END PRODUCTS

Raw Material	Intermediates	End Products
Methane	H_2	Fertilizer, explosives
	$CO + H_2$	Antifreeze, plastics
	HCN	Acrylic compounds
	C_2H_2	Vinyl compounds, resins
	Acrylonitrile	Fibers, resins, rubber
Ethane	C_2H_2	Plastics, fibers, additives, antifreeze, rubber, detergents
Propane	C_3H_6 Aldehydes Ketones Alcohols	Explosives, detergents, lacquers, solvents,
Butane	C_4H_8 C_4H_6	Rubber, nylon, oil additives, resins
Crude Oil	C_3H_6 C_4H_8 Benzene Toluene Styrene	Resins, rubbers, explosives, plasticizers, plastics.

Without attempting to cover the whole field a few typical examples may be analyzed. Using methane as a source of hydrogen for ammonia and ammonium nitrate production, it takes only about 0.6 lbs. of natural gas to produce 1.0 lb. of nitrate. This then appears to be a market-oriented industry. For making methanol the ratio is about 1.0, still in the range of market-oriented processes. However, if methanol is to be used as an intermediate for plastics, like urea-formaldehyde, involving several more chemical steps, then the over-all process could very well be raw-material-oriented.

The manufacture of acrylonitrile seems to be definitely raw-material-oriented if the acetylene-HCN route is used. Over 5 lbs. of natural gas are required to produce 1 lb. of acrylonitrile. The latter is a very promising chemical intermediate and a Western Canadian location does seem indicated.

Ethylene is by far the most important chemical intermediate in the whole synthetic organic industry. The American picture indicates a shift from refinery gases to natural gases as primary sources of ethylene; but it is uncertain whether it would be more economical to extract the ethane from the natural gas at the source or along a pipeline. However, in the past several years ethane extraction plants have been built at or near the terminals of long pipelines.

Propane, as a raw material source for petrochemicals, may be oxidized directly or converted into propylene. The construction of a large plant in Alberta by the Canadian Chemical Company, using the partial oxidation process, is clear evidence that under certain circumstances, the availability and low price of propane (and butane) outweigh other considerations in plant location. While propylene is an important petrochemical intermediate, it seems likely that for the next few years the demands can be satisfied by refineries.

The main petrochemical use for butane, at least in Canada, is for making butadiene, which is in turn used in the manufacture of synthetic rubber. The Polymer Corporation has indicated an interest in establishing a plant in Alberta for producing butadiene from the large quantities of butane that are expected to be made available when large scale gas export

becomes a reality. In this case, the prime consideration is a large and continuing raw material source.

Conclusions

The previously discussed factors may now be assessed to determine the degree to which they will influence the development of petrochemical industry in Alberta. The following observations may be made.

1. Not all petrochemical industries, not even those based on natural gas, are going to locate in Alberta. With the expected construction of gas pipelines, it may be more profitable to locate plants along the pipeline. It cannot be expected that all the petrochemical industries will be established in Alberta even if certain components of natural gas, namely propane and butane, are extracted at the source. In a very real sense, the whole natural gas hydrocarbon stream, including methane, consists of potential chemical raw materials. And once this gas leaves the Alberta border, it would be difficult if not impossible to control its end use. Ammonia from natural gas is one example of a market-oriented process and there seems little doubt that in the future ammonia plants will be built outside Alberta, using Alberta gas. Possibly the production of ethylene from ethane in pipeline gas is another market-oriented process. The National Petrochemical plant at Tuscola, Illinois, extracts ethane from natural gas originating about a thousand miles away, and there the ethane content of the gas is approximately the same as that of the gas that will be exported from Alberta.

Therefore, the construction of gas pipelines means that in the future a greater variety of potential sites will be available on which

to locate a petrochemical plant. As a consequence, all of Western Canada may participate in new petrochemical ventures. It would seem logical that in the years to come, particularly for chemical products that are to be exported, Vancouver as a site will receive a great deal of consideration.

2. There are some petrochemical industries, for which it makes good economic sense to locate in Alberta. And there are enough of these industries so that we can look forward to a considerable expansion of petrochemical manufacturing facilities in Alberta.